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Handbook for Sampling and Sample Preservation of Water and Wastewater

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This research program was initiated with the overall objective of providing guidelines for sampling and sample preservation of waters and wastewaters.

Information obtained from a review of the literature and the results of a survey of field practices provides the basis for guidelines in general sampling techniques, automatic samplers, flow measuring devices, a statistical approach to sampling, preservation of physical, chemical, biological and radiological parameters, and sampling procedures for waters emanating from municipal, industrial, and agriculture sources. Sampling procedures for surface waters and sludges are also included.

This report is not an official EPA manual. Rather, it is a research report which is but one of a series being used as an input to develop *EPA Manuals and Guidelines*.

This report was submitted in fullfillment of Contract No. 68-03-2075 by Envirex, Inc., A Rexnord Company, under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period of June 28, 1974 to June 1, 1976.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati engages in the following activities:

- Develops and evaluates techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigates methods for the concentration, recovery and indentification of viruses, bacteria, and other microbiological organisms in water. Conducts studies to determine the responses of aquatic organisms in water.
- Conducts an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

Standardized procedures for analyses of quality control become academic if samples are not representative of their original environment or if changes of constituent concentrations occur between time of sampling and analysis. This handbook presents techniques for sampling and sample preservation to help alleviate these problems. Procedures have been standardized as much as possible throughout this document. However, sampling techniques could not be predetermined for all situations, so the use of statistical procedures to establish location and frequency of sampling, number of samples, and parameters to be analyzed is recommended when other guidelines do not exist. Sample preservation methods and holding times are included for the 71 parameters listed for the NPDES program and selected biological species. Special handling or sampling techniques are also included for the individual constituents. Personnel establishing a sampling program should find sufficient information to determine the best techniques to apply. The justification for the recommended practices in this handbook are included in a research report that surveyed current field practices and available literature on sampling and sample preservation techniques. Further information can be obtained from this document entitled "Development of Guidelines for Sampling and Sample Preservation of Water and Wastewater."

This report is not an official EPA manual. Rather, it is a research report that is but one of a series being used as an input to develop *EPA Manuals and Guidelines*.

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CONTENTS

	PAGE
Foreword	iii
Abstract	iv
Figures	ix
Tables	xiv
Acknowledgments	xvii
1. Introduction	1
2. General Considerations For Sampling	3
2.1 Objectives of Sampling Programs	3
2.2 Type of Sample	4
2.3 Automatic Samplers	10
2.4 Flow Measurement with Sampling	18
2.5 Practical Features of Sampling	37
2.6 References	39
3. General Considerations of Sampling Preservation and Handling	41
3.1 Universal Preservation	41
3.2 Sample Identification	42
3.3 Chain of Custody	43
3.4 Container Type and Cleaning	53
3.5 Holding Time	57
3.6 Volume of Sample	57
3.7 Reference	58

CONTENTS (Continued)

		PAGE
4.	The Statistical Approach to Sampling	61
	4.1 Basic Statistics and Statistical Relationships.	61
	4.2 Determination of Number of Samples	78
	4.3 Determination of Sampling Frequency	84
	4.4 Determination of Parameters to Analyze	92
	4.5 In-Plant Sampling and Network Monitoring	102
	4.6 References	119
5.	Sampling Municipal Wastewaters	123
	5.1 Background	123
	5.2 Objectives of Sampling Programs	123
	5.3 Frequency of Sampling	123
	5.4 Location of Sampling Points	124
	5.5 Number of Samples	129
	5.6 Parameters to Measure	129
	5.7 Type of Sample	130
	5.8 Method of Sampling	130
	5.9 Automatic Samplers	130
	5.10 Volume of Sample and Container Type	131
	5.11 Preservation and Handling the Samples	131
	5.12 Flow Measurement	131
	5.13 References	131
6.	Sampling Industrial Wastewaters	133
	6.1 Background	133
	6.2 Objectives of Sampling Programs	133
	6.3 Frequency of Sampling	134
	6.4 Location of Sampling Points	135
	6.5 Number of Samples	135
	6.6 Parameters to measure	137
	6.7 Type of Sample	137
	6.8 Method of Sampling	140
	6.9 Automatic Samplers	142
	6.10 Volume of Sample and Container Type	143
	6.11 Preservation and Handling of Samples	143
	6.12 Flow Measurement	143
	6.13 References	144
7.	Sampling Surface Waters and Bottom Sediments	145
	7.1 Background	145
	7.2 Objectives of the Study	145
	7.3 Parameters to Analyze	145

CONTENTS (Continued)

		PAGE
7.4	Location of Sampling Points	146
7.5	Number of Samples	150
7.6	Frequency of Sampling	153
7.7	Method of Sampling	153
7.8	Types of Samples	153
7.9	Volume of Sample and Container Type	161
7.10	Preservation and Handling of Sample	161
7.11	Flow Measurement	161
7.12	References	161
8.	Sampling Agricultural Discharges	169
8.1	Background	169
8.2	Objectives	169
8.3	Frequency of Sampling	169
8.4	Location of Sampling Points	170
8.5	Number of Samples	170
8.6	Parameters to Analyze	170
8.7	Type of Sample	171
8.8	Method of Sampling	171
8.9	Volume of Sample and Container Type	174
8.10	Flow Measurement	174
8.11	References	174
9	Sampling Sludges	177
9.1	Background	177
9.2	Objectives of Sampling Programs	177
9.3	Parameters to Analyze	178
9.4	Location of Sampling Points	178
9.5	Frequency of Sampling	180
9.6	Number of Samples	181
9.7	Type of Sample	181
9.8	Method of Sampling	181
9.9	Volume of Sample and Container Type	181
9.10	Preservation and Handling of Samples	181
9.11	Flow Measurement	181
9.12	References	182
10.	Sample Preservation and Handling by Parameter Group	183
10.1	Introduction	183
10.2	Methods for Nutrients Parameter Group	183
10.3	Methods for Demand Parameter Group	194

CONTENTS (Continued)

		PAGE
10.4	Methods for Metals Parameter Group.....	202
10.5	Methods for Physical/Mineral Parameter Group.	207
10.6	Methods for Pesticides/Herbicides Parameter Group.....	220
10.7	Methods for Biological Group.....	229
10.8	Methods for Radioactive Parameter Group.....	232
10.9	References.....	242
11	Collecting and Handling Microbiological Samples.....	247
11.1	Background.....	247
11.2	Common Analyses.....	247
11.3	Sample Bottle Preparation.....	249
11.4	Sample Collection.....	250
11.5	Sample Preservation and Handling.....	252
11.6	References.....	254
Index	.....	255

FIGURES

NUMBER		PAGE
2.1	Volume and Time of Discrete Sample Collection for Four Periodic Compositing Methods	6
2.2	Example of Flow Proportional Sample Installation	17
2.3	Flow Measurement Devices for Filled Pipe Under Pressure	21
2.4	Techniques for Pipes Discharging to the Atmosphere	22
2.5	Sharp Crested Weir	26
2.6	Flow Rates in gallons per minute for 60° and 90° V-Notch Weirs	27
2.7	Nomograph for Capacity of Rectangular Weirs	28
2.8	Nomograph to Determine Fee Flow Through 3-inch to 8-ft Parshall Flumes	31
2.9	Parshall Flume	32
3.1	Chain of Custody Record Tag	44
3.2	Gummed Seal for Sample Bottles	45
3.3	Bottle Sample Tag Used by NFIC - Denver	46
3.4	Example of a Field Log Sheet	48
3.5	Chain of Custody Record Form	49
3.6	Sample Transmittal Form	51
4.1	Statistical Components of a Water Quality Record	62
4.2	Gaussian or Normal Distribution	66

FIGURES (Continued)

NUMBER		PAGE
4.3	Pearson Type III Probability Distribution and Density	68
4.4	Graphical Method for Determining Probability Distribution	74
4.5	Histogram and Probability Curve for Larger Number of Samples	76
4.6	Determination of the Number of Samples Based on the Required Accuracy of Extreme Values	82
4.7	Determination of the Number of Samples Based on the Required Accuracy of the Mean	85
4.8	Various Power Spectra for Variable X(t)	86
4.9	Determination of Sampling Frequency	88
4.10	Time Record of TOC of Municipal Wastewater, Racine, Wisconsin	90
4.11	Power Spectrum of TOC Concentration of Municipal Wastewater at Racine, Wisconsin	90
4.12	Power Spectrum of Chemical Plant Discharge, Case 1	91
4.13	Power Spectrum of Chemical Plant Discharge, Case 2	92
4.14	Relationship of TOC-BOD Concentrations of a Municipal Wastewater	96
4.15	Segmentation of a Wastewater System	103
4.16	An Industrial Water/Wastewater System	106
4.17	Linear Graph Representation of an Industrial Water/ Wastewater System	107
4.18	Estimation of Variability and Correlation in Segments	109
4.19	Correlogram for Segments	116
4.20	Spectral Analysis Computer Program	121

FIGURES (Continued)

NUMBER		PAGE
6.1	Factors of Plant Operation to be Considered in the Design of the Sampling Program	136
7.1	Example of the Transect Sampling Scheme	148
7.2	Example of Grid Sampling Scheme	149
7.3	Use of Spatial Gradient Technique for Maximum Spacing of Sampling Stations	150
7.4	Water Bottles	160
7.5	Bottom Grab Samplers	162
7.6	Core Samplers	164
7.7	Nets and Related Samplers	165
7.8	Periphyton Samplers	167
7.9	Macroinvertebrate Sampler	168
8.1	View of Field Installation	172
8.2	View of Field Installation	173
8.3	Schematic of Water Level Recorder and Sampler Arrangement	174
9.1	Recommended Minimum Sampling Programs for Municipal Wastewater Sludge Treatment Processes	179
10.1	Recommended Preservation and Handling Methods-TKN	187
10.2	Recommended Preservation and Handling Methods-NH_3	190
10.3	Recommended Preservation and Handling Methods-NO_3	191
10.4	Recommended Preservation and Handling Methods-NO_2	192
10.5	Recommended Preservation and Handling Methods NO_2/NO_3	193

FIGURES (Continued)

NUMBER		PAGE
10.6	Recommended Preservation and Handling Methods-Ortho Phosphate	193
10.7	Recommended Preservation and Handling Methods-Total Phosphate	195
10.8	Recommended Preservation and Handling Methods-BOD	198
10.9	Recommended Preservation and Handling Methods-COD	199
10.10	Recommended Preservation and Handling Methods-TOC	200
10.11	Recommended Preservation and Handling Methods-DO	201
10.12	Recommended Preservation and Handling Methods-As and B.	204
10.13	Recommended Preservation and Handling Methods-Ca, K, Na and Cr VI	205
10.14	Recommended Preservation and Handling Methods-Hg and Ag	206
10.15	Recommended Preservation and Handling Methods-Metals	208
10.16	Recommended Preservation and Handling Methods-Br^- and Cl	212
10.17	Recommended Preservation and Handling Methods-CN^- and F^-	213
10.18	Recommended Preservation and Handling Methods-$SO_4^=$ and $S^=$	215
10.19	Recommended Preservation and Handling Methods-$SO_3^=$ and Acidity	216
10.20	Recommended Preservation and Handling Methods-Alkalinity and Cl_2 Res	217
10.21	Recommended Preservation and Handling Methods-Color and Hardness	218
10.22	Recommended Preservation and Handling Methods-Oil and Grease and pH	221

FIGURES (Continued)

NUMBER		PAGE
10.23	Recommended Preservation and Handling Methods-Phenolics and Sp cond	222
10.24	Recommended Preservation and Handling Methods-Surfactant and Turbidity	223
10.25	Recommended Preservation and Handling Methods-Total and Volatile Solids	224
10.26	Recommended Preservation and Handling Methods-SS and TDS	225
10.27	Recommended Preservation and Handling Methods-Pesticides and PCB's	228
10.28	Recommended Preservation and Handling Methods-Benzidine	240
10.29	Recommended Preservation and Handling Methods-Radioactive	241
11.1	Recommended Preservation and Handling Methods-Microbiological Parameters	253

TABLES

NUMBER		PAGE
2.1	Time of Collection and Volume of Samples for the Four Compositing Methods	5
2.2	Advantages and Disadvantages of Methods of Compositing	7
2.3	Manual Preparation of Volume Variable Composite	9
2.4	Automatic Samplers and Their Features	11
2.5	Flow Measurement in Pressure Pipes	19
2.6	Advantages and Disadvantages of Flumes and Weirs	33
2.7	Advantages and Disadvantages of Secondary Devices	34
2.8	Relative Comparison of Primary and Secondary Open Channel Flow Measurement Devices	35
3.1	Comparison and Glass and Plastic Containers	54
3.2	Comparison of Cap Liners	55
4.1	Areas Under Standardized Normal Density Function	67
4.2	Percentage Points of Chi-Square Distribution	69
4.3	Percentage Points of Student Distribution	71
4.4	Computational Table for Graphical Normal or Pearson Type 111 Distribution Determination	73
4.5	K Values for Positive Skew Coefficients	79
4.6	K Values for Negative Skew Coefficients	80
4.7	Sampling Priorities of Parameters for a Typical Wastewater	94

TABLES (Continued)

NUMBER		PAGE
4.8	Values of Correlation Coefficient p, for Two Levels of Significance	99
4.9	Correlation Matrix of Coefficient, p x y p_{xy}	101
4.10	Wastewater Loads to Nodes	113
4.11	Coefficient of Variation in Branches	114
4.12	Determination of the Sampling Priorities of Segments	115
5.1	Process Testing Guide	125
5.2	Recommended Minimum Sampling Programs for Municipal Wastewater Treatment Processes	127
6.1	NPDES Effluent Limitation Parameters by Industry	138
6.2	Types of Composites for Different Discharges	140
6.3	The Advantages and Disadvantages of Manual and Automatic Sampling	141
6.4	Comparison of Requirements and Features of Automatic and Manual Methods	142
7.1	Common Analyses for Surface Water and Sediment Sampling	146
7.2	Model State Water Monitoring Program Guidelines for Biological Monitoring	154
7.3	Comparison of Water Samplers	155
7.4	Comparison of Bottom Grabs	156
7.5	Comparison of Coring Devices	157
7.6	Comparison of Net Sampling Devices	158
7.7	Comparison of Substrate Samplers	159
10.1	Parameter Group Classifications	184

TABLES (Continued)

NUMBER		PAGE
10.2	Partial Listing of Commercial Mercury Reprocessors.....	188
10.3	Atomic Absorption Concentration Ranges with Convention Atomization.....	203
10.4	Persistance of Pesticides Compounds in River Water.....	227
10.5	Parameters of Biological Communities Most Commonly Analyzed for Monitoring Purposes.....	231
10.6	Comparison of Chemical Preservatives for Biological Parameters.....	233
10.7	Recommended Preservation and Handling Methods-Benthic Macroinvertebrates.....	234
10.8	Recommended Preservation and Handling Methods-Fish.....	235
10.9	Recommended Preservation and Handling Methods-Macrophytes and Macroalgae.....	236
10.10	Recommended Preservation and Handling Methods-Periphyton.....	237
10.11	Recommended Preservation and Handling Methods-Phytoplankton.....	238
10.12	Recommended Preservation and Handling Methods-Zooplankton.....	239

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CHAPTER I

INTRODUCTION

Obtaining representative samples and then maintaining the integrity of the constituents is an integral part of any monitoring or enforcement program. Standardization of the analytical techniques has been established to a high degree but the result of analysis is only as good as the sampling and the sample preservation. The purpose of this handbook is to present the best techniques currently available for sampling and sample preservation. The recommendations were developed from an extensive research report (1) which included a literature review and survey of current laboratory and field practices. The handbook will allow the personnel to determine the most effective procedures for their specific applications.

In sampling, the objective is to remove a small portion of an environment that is representative of the entire body. It is then obvious that improper sampling will give erroneous results. Once the sample is taken, the constituents of the sample must stay in the same condition as when the sample was collected. The length of time that these materials will remain stable is related to the preservation method. Effective sample preservation will allow a sample's constituents to be preserved for longer periods of time.

The sampling technique is affected by the type of water or wastewater to be sampled. Therefore the following areas are addressed in this handbook:

1. Municipal wastewaters
2. Industrial wastewaters
3. Surface waters and sediments
4. Agricultural runoff
5. Wastewater sludges

General information on automatic samplers and flow monitoring is also included.

Statistical methods have been presented in this handbook and will be used to determine the following aspects of sampling programs:

1. Number of samples
2. Frequency of sampling
3. Location of sampling
4. Parameters to measure

Preservation methods are related to the parameters to be analyzed so, in this handbook, these techniques are classified by parameter. The (71) parameters specified for the NPDES permit program in the Federal Register, of October 16, 1973, and selected biological parameters are included.

CHAPTER 2

GENERAL CONSIDERATIONS FOR SAMPLING

There are certain areas of sampling which apply to all types of waters and wastewaters including:

1. Objectives of Sampling Programs
2. Type of Sample
3. Automatic Samplers
4. Flow Measurement with Sampling
5. Practical Features of Sampling

2.1 OBJECTIVES OF SAMPLING PROGRAMS

The objectives of a program directly affect all aspects of sampling and the analyses performed on the sample. Therefore, determination of objectives is the first decision when establishing a sampling program.

2.1.1 Regulatory Objectives

Sampling and subsequent analyses are often performed to meet the requirements of state, federal or local regulatory agencies. The self-monitoring is then enforced by agencies to assure compliance with the regulations. An example is the National Pollutant Discharge Elimination System (NPDES) which issues a permit to discharge to surface waters.

Often the details of sampling including number of samples, frequency, parameters to analyze and location are specified in the permit. However, other important details such as type of composite are not included. Compliance with regulatory objectives means that any previously specified standards be followed.

2.1.2 Research Objectives

To evaluate the effectiveness of research projects, sampling must be done at the influent and effluent to a certain process. The program of sampling may be simple or complex depending on the project. Standard sampling techniques using the best available technology are critical for establishing comparable and valid data.

2.1.3 Process Control Objectives

Standardization of inplant sampling for process control is necessary for comparable data or regulatory compliance. The determination of efficiency of a unit process, whether treatment or production, is a process control objective.

2.2 TYPE OF SAMPLE

2.2.1 Grab Samples

A grab sample is defined as a single sample taken at a point in time. It can be taken using a pump, scoop, vacuum, or other suitable device. The use of a pump over a short time period (fifteen minutes or less) often is convenient. The collection of a grab sample is appropiate when it is desired to:

1. Characterize water quality at a particular time
2. Provide information about minimum and maximum
3. Allow collection of variable sample volume

2.2.2 Composite Samples

A composite sample is defined as a sample formed by mixing discrete samples taken at periodic points in time or a continuous portion of the flow. A sequential composite is defined as a series of short period grab samples each of which is held in an individual container, then composited to cover a longer time period. Six methods are used for forming composites:

Method No.	Sampling mode	Compositing principle
1	Continuous	Constant sample pumping rate
2	Continuous	Sample pumping rate proportional to stream flow
3	Periodic	Constant sample volume, constant time interval between samples
4	Periodic	Constant sample volume, time interval between samples proportional to stream flow
5	Periodic	Constant time interval between samples, sample volume proportional to total stream flow since last sample
6	Periodic	Constant time interval between samples, sample volume proportional to stream flow at time of sampling

Compositing on the basis of flow is necessary because this procedure will provide a representative mass loading of the discharge on a receiving water for the period sampled.

To illustrate the differences between the periodic composite samples, the following example is given.

> Example - It is desired to determine the average characteristics of an industrial discharge over an 8 hour working day. The flow varies as shown in Figure 2.1. Approximately 4 liters (1.1 gal.) of a composite sample are needed by the laboratory for analyses. Assuming eight samples are collected over the day, the time of collection and volume of each sample used for the composite are shown in Figure 2.1 and given in Table 2.1 for the four types of periodic compositing methods.

Table 2.1. TIME OF COLLECTION AND VOLUME OF SAMPLES FOR THE FOUR COMPOSITING METHODS

Sample No.	Time of sampling, hr composite method no.				Volume of sample, ml composite method no.			
	3	4	5	6	3	4	5	6
1	1.0	1.8	1.0	1.0	500	500	160	302
2	2.0	2.7	2.0	2.0	500	500	420	560
3	3.0	3.4	3.0	3.0	500	500	660	735
4	4.0	4.0	4.0	4.0	500	500	760	795
5	5.0	4.6	5.0	5.0	500	500	760	735
6	6.0	5.3	6.0	6.0	500	500	660	560
7	7.0	6.2	7.0	7.0	500	500	420	302
8	8.0	8.0	8.0	8.0	500	500	160	0

In methods 3, 5, and 6, there is a constant time interval between sampling periods. In method 4, the interval is variable and dependent on the time needed for a given volume of flow to pass. A sample is therefore taken each time 1,250 l (330 gal.) passes.

2.2.3 Selection of Sample Type

Use grab samples when (1,2,3)

1. The stream does not flow continuously (i.e. batch dump).
2. The water or waste characteristics are relatively constant (i.e. sludge).

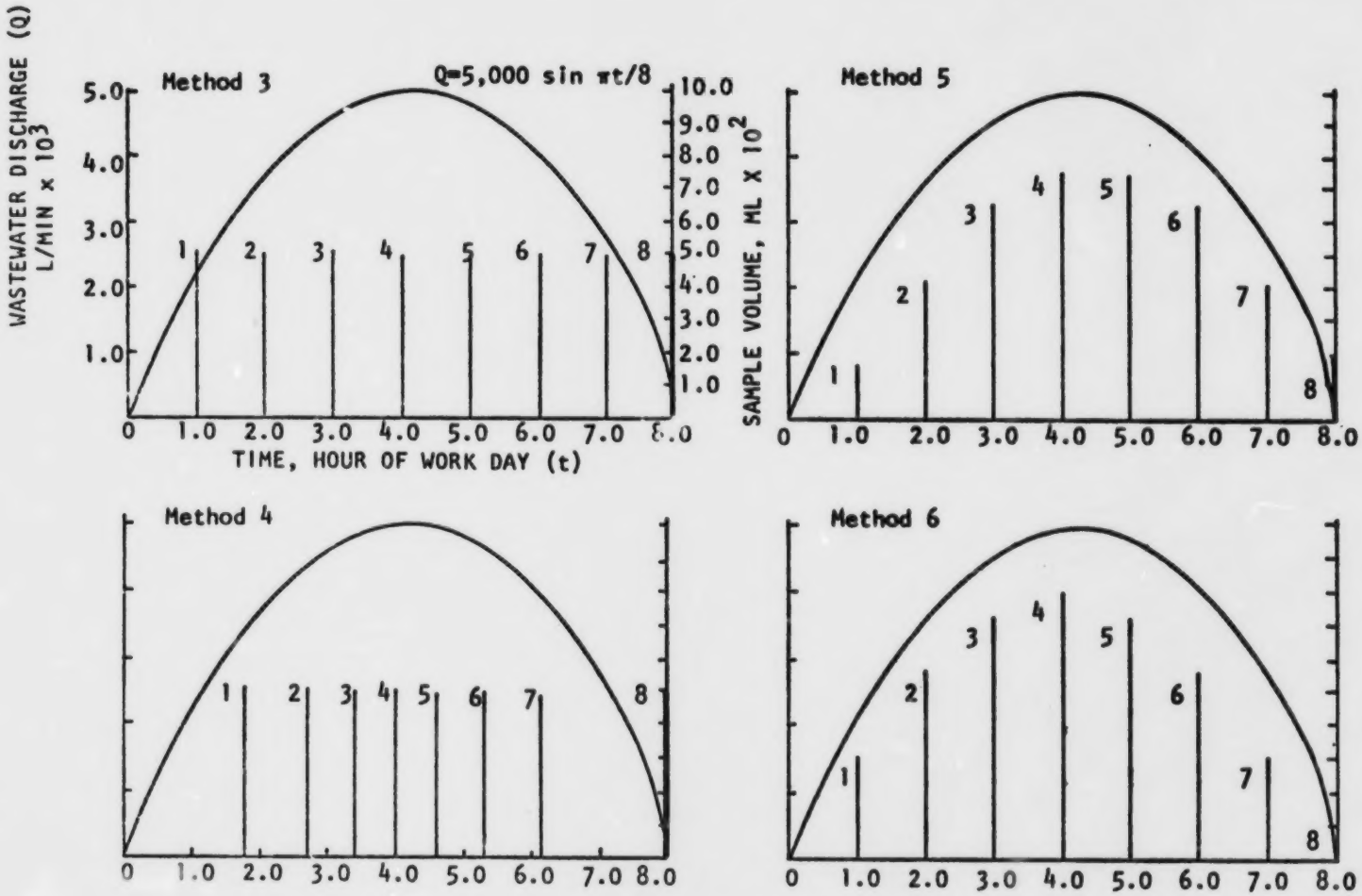


Figure 2.1. Volume and time of discrete sample collection for four periodic compositing methods

3. The parameters to be analyzed are likely to change (i.e. dissolved gases, residual chlorine, soluble sulfide, oil and grease, microbiological parameters, etc.).

4. The maximum or variability is to be determined.

5. The history of water quality is to be established based on relatively short time intervals.

Use composite samples when

1. Determining average waste concentrations.

2. To calculate mass/unit time loading.

2.2.4 Selection of Composite Type

Choice of composite type is dependent on the program and the advantages and disadvantages of each is given in Table 2.2.

Table 2.2 ADVANTAGES AND DISADVANTAGES OF METHODS OF COMPOSITING

Compositing method	Advantages	Disadvantages
Continuous		
1. Constant sample pumping rate	Minimal manual effort; requires no flow measurement	Requires large sample capacity, or small pump which may clog; may lack representativeness especially for highly variable flows; requires power.
2. Sample pumping rate proportional to stream flow	Most representative especially for highly variable flows; minimal manual effort.	Requires accurate flow measurement/recording equipment; requires large sample volume; or small pump which may clog; requires variable pumping capacity; requires power.
3. Constant sample volume, constant time interval between samples	Minimal instrumentation and manual effort; requires no flow measurement	May lack representativeness especially for highly variable flows

Table 2.2. (continued). ADVANTAGES AND DISADVANTAGES OF METHODS OF COMPOSITING

Compositing method	Advantages	Disadvantages
4. Constant sample volume, time interval between samples proportional to stream flow	Minimum manual effort	Requires accurate flow measurement/recording equipment
5. Constant time interval between samples, sample volume proportional to total stream flow since last sample	Minimal instrumentation	Manual compositing from flow chart
6. Constant time interval between sample, sample volume proportional to total stream flow at time of sampling	Minimal instrumentation	Manual compositing from flow chart

2.2.5 Method of Compositing

The preparation of the flow rated composite is performed in various ways. Table 2.3 summarizes the techniques necessary for preparing composites from time constant, volume variable samples.

When using a volume constant, time proportional compositing method, previous flow records should be used to determine an appropriate flow volume increment so a representative sample is obtained without overrunning the bottle capacity or supply.

Table 2.3 MANUAL PREPARATION OF VOLUME VARIABLE COMPOSITE

Type	Preparation	Equation
Time const/volume prop. to flow since last sample	Determine volume since last sample by integration	$V_d = \frac{F_s}{F_t} V_c$ V_d = discrete sample vol. V_c = composite vol. (known) F_s = flow volume since last sample (integration) F_t = total flow volume (estimated)
Time const, volume prop. to instantaneous flow rate	Note flow rate at each time of discrete sample collection	$ax + bx + cx = V_c$ a,b,c = flow rates when samples taken (noted) x = volume sample/unit flow (desired) V_c = composite volume (known) $V_d = \frac{V_c}{n}$ V_d = discrete sample vol. (desired) V_c = composite volume (known) n = no. of discrete samples

2.3 AUTOMATIC SAMPLERS

2.3.1 Background

Use of automatic samplers has been increasing to implement the NPDES self-monitoring requirements. The following advantages are apparent (4):

1. Eliminates inevitable errors due to the human element in manual sampling.

2. Reduces to a minimum costly personnel requirements.

3. Eliminates a routine task which can devolve into an irksome chore.

4. Provides the capability for more frequent sampling than is practical for manual sampling.

There are many commercial samplers (see Table 2.4). However, no single automatic sampling device is ideally suited for all situations. For each application these variables should be considered (5):

1. Variation of water or wastewater characteristics with time.

2. Variation of flow rate with time.

3. Specific gravity and concentrations of suspended solids.

4. Presence of floating materials.

The following list of functional subsystems is intended to aid in the proper selection and use of an automatic sampler.

2.3.2 Criteria for Evaluating Sampler Subsystems

2.3.2.1 Intake Device -

1. Causes minimum obstruction of sewer or channel to minimize chances of fouling or damage.

2. Is capable of drawing a sample representative of entire stream flow (including surface, middle and bottom layers) (6). Use of multiple intakes may be warranted (5).

3. Is resistant to plugging by providing coarse screening if large materials such as rags, sticks, and stones are present (5). However, smaller suspended solids should not be excluded by the intake.

Table 2.4. AUTOMATIC SAMPLERS AND THEIR FEATURES

Sampler	Method of sample transport	Refrigeration provided	Ability to withstand		Ability to sample		Self-cleaning features
			Freezing	Immersion	Floatables	Coarse bottom sediments	
BIF	Dipper	yes	no	no	no	no	none
Brailsford DC-F	Positive displacement pump	no	no	no	no	no	continuous flow
Brailsford EV-F	Vacuum pump	no	no	no	no	no	backflush
BVS PP-100	Pneumatic ejection	yes	yes	no	yes	no	air purge
BVS SE-400	Submersible pump	yes	yes	no	no	no	continuous
BVS SE-600	None provided - solenoid valve diversion from sample line[c]	yes	yes	no	b	b	continuous flow
Chicago "Tru-Test"	Dipper from sample chamber provided by customer	yes	no	no	b	b	continuous
Hydro-Numatic	Centrifugal pump	no	yes	no	b	b	continuous flow
Infilco	Dipper from sample chamber provided by customer[c]	yes	no	no	b	b	continuous flow
ISCO 1391	Peristaltic pump	ice cavity[e]	no	yes	yes	no	backflush
Lakeside T-2	Dipper	yes	no	no	some	some	none
Markland 1301[a]	Pneumatic ejection	no	yes	no	no	no	none
Markland 101[a]	Pneumatic ejection	yes	yes	no	no	no	none
Markland 102[a]	Pneumatic ejection	yes	yes	no	no	no	air purge
Markland 104T[a]	Pneumatic ejection	yes	yes	no	no	no	none
N-Con Surveyor	Centrifugal pump	no	no	no	no[d]	no[d]	gravity drain
N-Con Scout	Peristaltic pump	no	no	no	no	no	backflush
N-Con Sentry	Peristaltic pump	no	no	no	no	no	backflush
N-Con Trebler	Dipper	yes	no	no	some	some	none

a. Representativeness of sample questioned in Reference 5.
b. Depends on how user arranges sampler intake.
c. Continuous flow sample line provided by user.
d. Refrigeration provided only for stationary sampler.
e. Ice cavity has been reported to cool sample from 21°C to 4°C in 6 hours; additional housing with ice in 3 hours (10).

Table 2.4 (continued). AUTOMATIC SAMPLERS AND THEIR FEATURES

Sampler	Method of sample transport	Refrigeration provided	Ability to Withstand		Ability to sample		Self-cleaning features
			Freezing	Immersion	Floatables	Coarse bottom sediments	
N-Con Sentinel	Dipper from sample chamber provided by customer[c]	yes	no	no	b	b	continuous flow
Phipps & Bird	Dipper	no	no	no	no	no	none
Protech CG-125[e]	Pneumatic ejection	yes	yes	no	no	no	backflush
Protech CG-125FP[e]	Pneumatic ejection	d	yes	no	no	no	backflush
Protech CG-150[e]	Pneumatic ejection	d	yes	no	no	no	backflush
Protech CEL-300	Submersible pump	d	yes	no	no	no	continuous flow
Protect DEL-2405	Submersible pump	yes	yes	no	no	no	continuous flow
QCEC CVE	Vacuum pump	yes	yes	no	no	no	air purge
QCEC E	Dipper	no	no	no	no	no	none
SERCO NW-3	Evacuated bottles	ice cavity[e]	no	no	no	no	none
SERCO TC-2	Dipper from sample chamber provided by customer[c]	yes	no	no	b	b	continuous flow
Sigmamotor WA-1[e]	Peristaltic pump	yes	no	no	no	no	backflush
Sigmamotor WA-3[e]	Peristaltic pump	no	no	no	no	no	none
Sigmamotor WDPP-2[e]	Peristaltic pump	no	no	no	no	no	none
Sigmamotor WM-1-24	Peristaltic pump	yes	no	no	no	no	backflush
SIRCO BST-VS	Vacuum pump	yes	yes	no	b	b	backflush
SIRCO B/IE-VS[e]	Dipper	yes	yes	no	no	no	none
SIRCO B/DP-VS	None provided - solenoid valve diversion from sample line	yes	yes	no	no	no	continuous flow
SIRCO PII-A	Vacuum pump	no	no	no	b	b	backflush

a. Representativeness of sample questioned in Reference 5.
b. Depends on how user arranges sampler intake.
c. Continuous flow sample line provided by user.
d. Refrigeration provided only for stationary sampler.
e. Ice cavity has been reported to cool sample from 21°C to 4°C in 6 hours; additional housing with ice in 3 hours (10).

Table 2.4 (continued). AUTOMATIC SAMPLERS AND THEIR FEATURES

Sampler	Method of sample Transport	Refrigeration provided	Ability to withstand Freezing	Ability to withstand Immersion	Floatables	Coarse bottom sediments	Self-cleaning features
Sonford HG-4[a]	Sample tube which fills by gravity	ice cavity[e]	no	no	no	no	none
TNI	Pneumatic ejection	no	yes	no	no	no	none
TNI Mark 38	Evacuated bottles	no	no	no	no	no	none
AVCO[d]	Peristaltic pump	no	no	no	some	no	none
Springfield	Dipper from sample chamber provided with continuous flow by screwrotor pump	yes	no	no	some	some	continuous flow
Milk River	Submerged pump	yes	--	--	--	--	--
Envirogenics	Mechanical - gravity	no	yes	yes	yes	yes	no
Rohrer I	Diaphragm pump	no	yes	no	b	b	continuous flow
Weston	Evacuated bottle from sample chamber provided with continuous flow	yes	no	no	b	b	continuous flow
Pavia-Byrne	Screw pump	yes	no	no	no	no	continuous flow
Rexnord	Positive displacement pump	no	no	no	b	b	backflush
Colston	Serco HV-3 samples from a flume provided with continuous flow	no	no	no	no	no	none for SERCO par
Rohrer II	Diaphragm pump	no	yes	no	b	b	continuous flow
Hoar	Piston in tube	no	no	no	yes	no	[illegible]
Freeman	None provided - solenoid valve diversion from sample line[c]	no	yes	no	b	b	continuous flow

a. Representativeness of sample questioned in Reference 5.
b. Depends on how user arranges sampler intake.
c. Continuous flow sample line provided by user.
d. Refrigeration provided only for stationary sampler.
e. Ice cavity has been reported to cool sample from 21° to 4°C in 6 hours; additional housing with ice in 3 hours (10).

4. Is firmly secured or anchored at permanent installations.

2.3.2.2 Sample Transport -

1. Sample line minimum size is 0.6 cm (1/4 in.) internal diameter (5).

2. Sample must not contact metals during transport.

3. Sample line must be transparent and flexible, and made of an inert material such as Tygon[R]. If trace quantities are to be measured, a method of testing for tube contamination is needed (8).

4. Purging of the sample line should be done between sample collections. A clean water purge is effective (5) but not feasible in most instances. A complete air purge is sufficient for non-permanent or winter operation. A final alternate is a sample purge prior to collection.

2.3.2.3 Sample Collection - The sample collection device should meet the following criteria unless the specific application does not require it.

1. Capable of lifting a sample a vertical distance (head) of 6.1 m (20 ft) (7).

2. Capable of maintaining a line velocity of 0.6 to 3.0 m/sec (2-10 ft/sec) for vertical transport (7).

3. Sample volume independent of distance of vertical lift (head).

The importance of line velocity and isokinetic conditions depends on the concentration and density of the nonfilterable suspended solids in the water and the program requirements for accuracy of suspended solids determinations and any other parameters affected by suspended solids concentrations. (See Chapter 5 for guidelines.) If the program requires maintaining isokinetic conditions, dial adjustment of the intake velocity should be included as a criterion.

2.3.2.4 Power and Controls - The following features should be available:

1. Capability for both AC and DC operation.

2. Battery life for 2 to 3 days of reliable hourly sampling without recharging (7).

3. Battery weight of less than 9 kg (20 lb) and sealed so no leakage occurs.

4. Solid state logic and printed circuit boards.

5. Timing and control systems are contained in a water-proof compartment and protected from humidity. Timer should use solid state logic and a crystal controlled oscillator.

6. Controls to allow both flow-proportional sampling (directly linked to a flow meter) and periodic sampling at an adjustable interval from 10 minutes to 4 hours (7).

7. Capability of multiplexing, i.e., drawing more than one sample into a discrete sample bottle to allow a small composite over a short interval (7). Also capability for filling more than one bottle with the same aliquot for addition of different preservatives.

2.3.2.5 Sample Storage -

1. Capability of discrete sample collection with provision for single composite container.

2. Minimum discrete sample container volume of 500 ml (0.13 gal.) and a minimum composite container capacity of 9.5 l (2.5 gal.)

3. Sampler capacity of at least 24 discrete samples.

4. Containers of conventional polyethylene or borosilicate glass, and of wide mouth construction.

5. Capability for cooling samples by refrigeration or a space for packing ice.

6. Insulation available if the sampler is to be used during freezing conditions.

2.3.2.6 General Desirable Features -

1. Water tight casing to withstand total immersion and high humidity.

2. Vandal-proof casing with provisions for locking.

3. A secure harness or mounting device if sampler is placed in a sewer.

4. Explosion-proof manufacture.

5. Sizing to fit in a standard manhole without disassembly.

6. Compact and portable for one-man installation.

7. Overall construction, including casing, of materials resistant to corrosion (plastics, fiberglass, stainless steel).

2.3.3 Installation and Use

2.3.3.1 General Consideration - Well-designed equipment will give good results only when properly maintained (see Figure 2.2).

1. When a sampler is installed in a manhole, secure it either in the manhole (e.g. to a rung) above the high water line or outside of the manhole (e.g. to an above ground stake by means of a rope).

2. Place the intake tubing vertically or at such a slope to ensure gravity drainage of the tubing between samples, avoiding loops or dips in the line.

3. Clean sample bottles, tubing and any portion of the sampler which contacts the sample between setups. Whatever methods of cleaning are used, all parts of the sampler which come in contact with the sample should be given a final rinse with tap water and with distilled water. A distilled water rinse may not be necessary between setups on the same waste stream.

4. Inspect the intake after each use, and clean if necessary. Care should be used in placing the intake(s) to assure a representative suspended solids sample. The velocity of flow should at all times be sufficient to prevent deposition of solids. When a single intake is to be used in a channel, place it at six-tenths depth (point of average velocity) (9, 20). For wide or deep channels where stratification exists, set up a sampling grid as described in Section 7.4.2.

5. Maintain electrical and mechanical parts according to the manufacturer's instructions. The desiccant should be replaced as needed. If a wet-cell lead-acid battery is used, any acid spilled should be neutralized and cleaned up.

6. Position the intake in the stream facing upstream. It should be secured by a rope at all times with no drag placed on the inlet tubing.

7. After the installation is complete, collect a trial sample to assure proper operation and sample collection. The sampler must give replicate samples of equal volume throughout the flow range. If the sampler imposes a reduced pressure on a waste stream containing suspended solids, run the first part of the sample to waste.

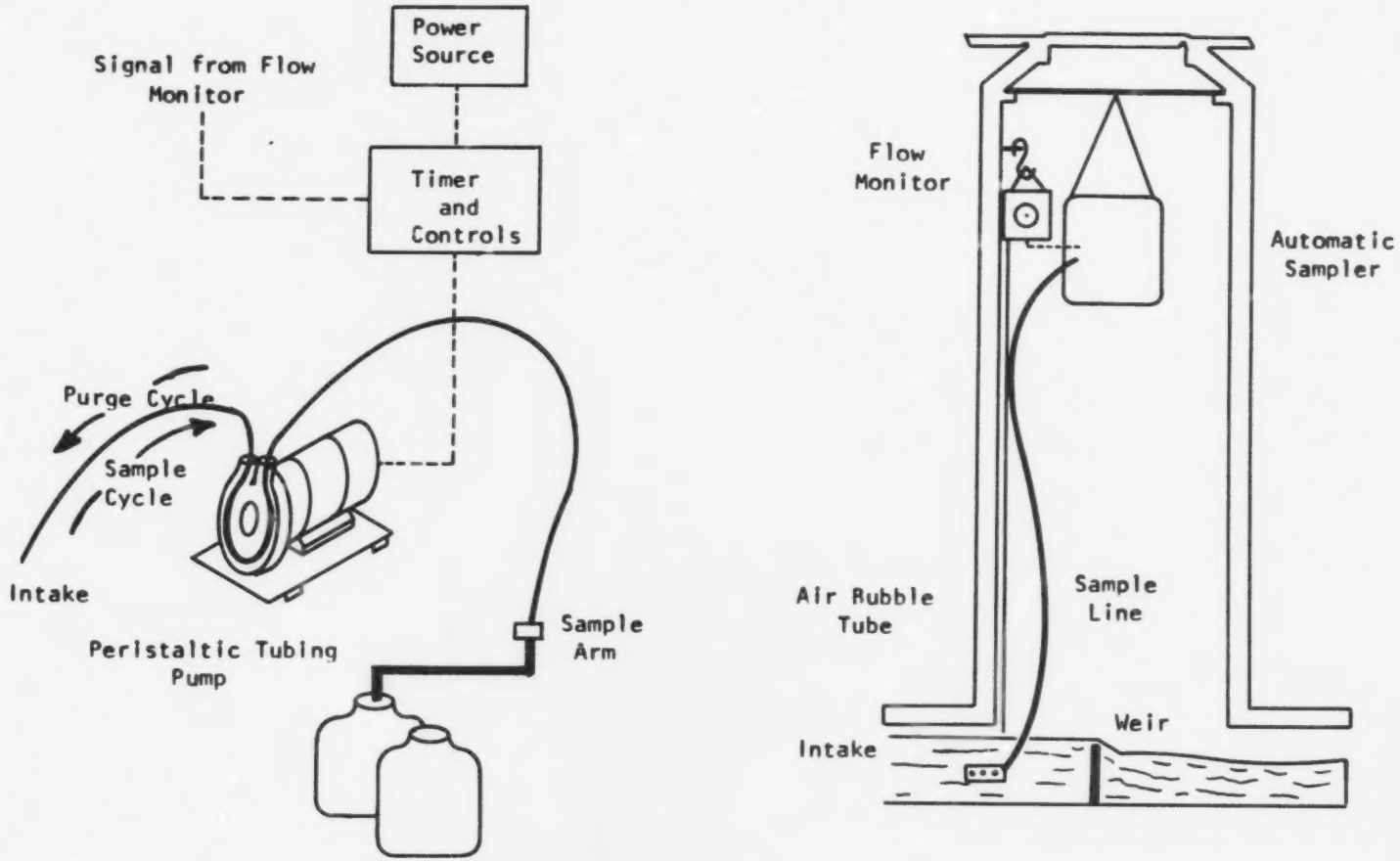


Figure 2.2. Example of flow proportional sampler installation

2.3.3.2 Winter Operation - For outdoor use in freezing temperatures special precautions should be used to insure reliable sample collection and to prevent the collected sample(s) from freezing.

1. Place the sampler below the freezing level or in an insulated box.

2. When AC is available, use a light bulb or heating tape to warm sampler. The following arrangement was found satisfactory between -18 and -12°C (0 and 10°F) (11):

   ...wrap short (4 or 6 ft thermostatically protected 38°F) heat tape around the sample bottle and the intake lines on the AC samplers. Over the heat tape on the intake loosely wrap a large plastic bag (airline trash bags, 10 mil, GSA #8105-808-9631). A large plastic bag should also be placed over the sampler as loosely as possible.

3. Be certain to place the line vertically or at such a slope to ensure gravity drainage back to the source. Even with a back-purge system some liquid will remain in the line unless gravity drainage is provided. If an excess length of tubing exists, this excess should be collected and placed in the water.

2.4 FLOW MEASUREMENT WITH SAMPLING

Flow measurement can be divided into four categories:

1. Flow in completely filled pipes under pressure.

2. Flow from pipes discharging to the atmosphere.

3. Flow in an open channel or sewer.

4. Miscellaneous flow measurement

This section will give an overview of flow measurement. Other manuals should be consulted for more information (12, 13, 14, 15).

2.4.1 Flow in Completely Filled Pipes Under Pressure

There are nine common types of flow measurement methods. Table 2.5 discusses the information required to apply each one, and Figure 2.3 gives a visual example of some typical designs.

Table 2.5. FLOW MEASUREMENT IN PRESSURE PIPES

Type	Equation	C_{value}	Accuracy	Advantages	Disadvantages	Linear Pipe Diameters Upstream
Orifice	$Q = CAK\sqrt{H}$	0.61 to 0.71 depends on d_2/d_1	1-2% (18)	Inexpensive, Easy to Install, Reliable	Large Head Loss, Solids Interference, Less accurate at high velocity	5-25 Diameters (14)
Venturi	$Q = CAK\sqrt{H}$	0.98	1-2% (18)	Low Pressure loss, No Interference from Solids	More Expensive, Requires more room	5-15 Diameters (13)
Flow Nozzle	$Q = CAK\sqrt{H}$ d_2 = diameter at outlet end of nozzle	.98 - .99	1-2% Good	Low Maintanence, Installable in Pipe Flanges, Less ΔP than Orifice, Moderate suspended Solids Allowed	High Velocity, No Burrs in Line	10 Pipe Diameter (12)
Pitot Tube	$V_c = C\sqrt{2gH}$ $Q = V_m A$ $V_m = .83\ V_{center}$	C = correction factor determined by calibration	Good	Good in Large Pipes, Less Expensive	Point Measure Only, Solids Pluggage a Problem	15 Diameters to 50 (13)
Magnetic Flowmeter	Direct Voltage Readout	----	1% at 3 to 30 fps Better at Higher velocities (13)	No Head Loss, No Solids Problem	Expensive, Can Be Fouled By Grease, Permanent	----
Ultrasonic Flowmeter	Direct Readout	----	Good in Certain instances	No Solids Problem	Air Bubbles Interference	----
Elbow Meters	$C\sqrt{K_c/2D}$	0.98 ± 6% if Turbulent	Good (Hydraulics)	No Fouling. Pressure Loss Minimized	Difficult to Calibrate	----

Table 2.5 (Continued). UNIT DESCRIPTION

Q = flow (cfs) (x 0.0283 = cu m/sec)

A = throat area (ft^2)

H = $H_1 - H_2$ differential head in (ft. of water)

H_1 = pressure head at center of pipe at inlet (ft. of water)

H_2 = pressure head at throat (ft. of water)

K = $$\sqrt{\frac{2g}{1 - \left(\frac{d_2}{d_1}\right)^4}}$$

g = gravity constant (32.2 ft./sec^2)

d_2 = throat diameter (ft.)

d_1 = diameter of inlet pipe (ft.)

R = radius of curvature of center line (ft.)

D = pipe diameter (ft.)

V = velocity (ft./sec) (x 0.305 = m/sec)

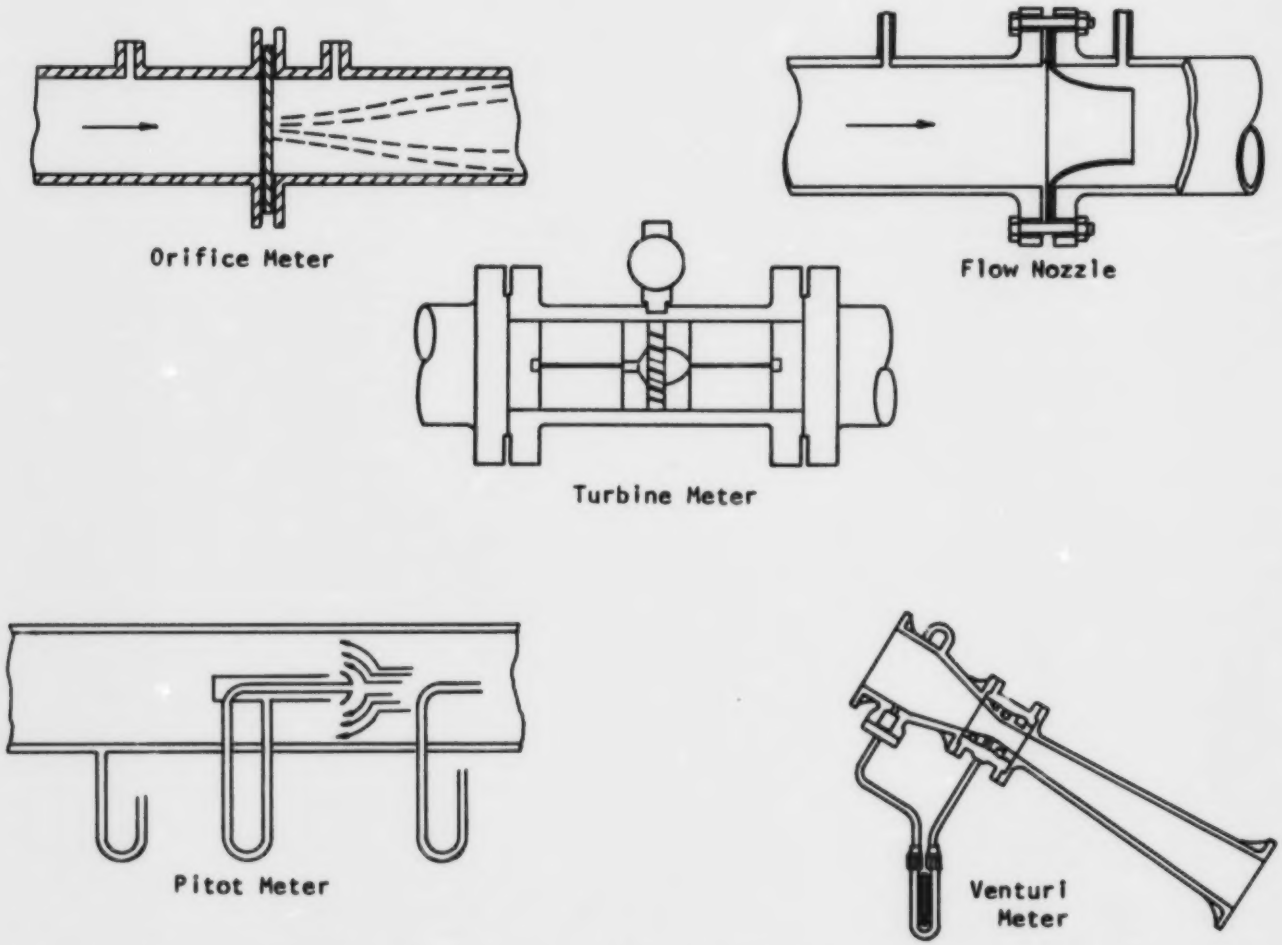


Figure 2.3. Flow measurement devices - filled pipe under pressure (12)

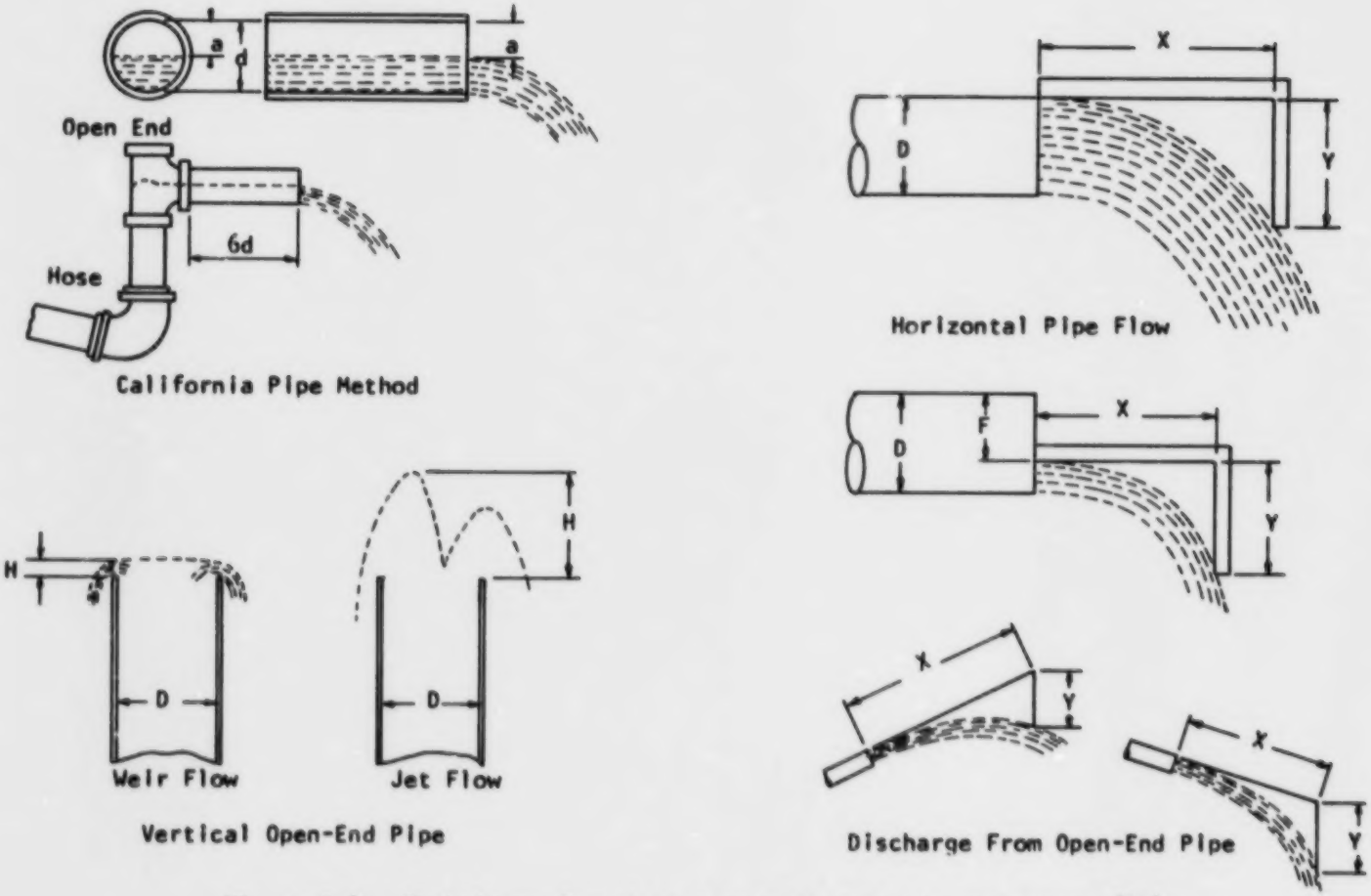


Figure 2.4. Techniques for pipes discharging to the atmosphere (12)

2.4.2 Flow from Pipes Discharging to the Atmosphere

The common techniques for measuring the flow from open ended pipes eithe full or partially full are listed below. Figure 2.4 indicates the systems described.

2.4.2.1 Flowing Full -

1. Orifice (12) $Q = CAK\sqrt{H}$ Units as before

2. Flow nozzle (12) $Q = CAK\sqrt{H}$ Units as before

3. Vertical open end pipe (12)

   a. Weir flow $Q = 8.80\ D^{1.20}\ H^{1.24}$

   b. Jet flow $Q = 5.84\ D^{2.025} H^{0.53}$

   where
   Q = flow, cfs (cu m/sec = cfs x 0.0283)
   D = internal pipe diameter, ft
   H = distance from pipe outlet to top of crest, ft

4. Rotating element meters

   a. Propeller meters (Ott, Sparling)

   where
   Q = f/k
   f = pulse frequency
   k = flow coefficient

   b. Cup type meters

5. Orifice (Danaides) bucket (16)

6. Horizontal or sloped open end (12)

$$Q = 0.008\ \frac{AX}{\sqrt{Y}}$$

Q = flow, cfs (cu m/sec = cfs × 0.0283)
A = cross sectional area (ft^2)
X = distance from end to where Y measured (in.)
Y = vertical top measured at X (in.)

2.4.2.2 Pipes Flow Partially Full -

1. Horizontal or sloped open ended (See Reference 12 for correction factor, Table 4.3)

$$Q = \text{corr. factor}\ \frac{0.008\ AX}{\sqrt{Y}}$$

2. California Pipe Method (12) $Q = TW$

$T = 8.69 \left(1 - \frac{a}{d}\right)^{1.88}$
$W = d^{2.48}$
d = pipe diameter (ft)
a = distance from top of pipe to flow (ft)
Q = cfs (cu m/sec = cfs x 0.0283)

3. Open Flow Nozzles - Various types are available (Kennison and parabolic flume). The manufacturer should be consulted.

2.4.3 Flow Measurement in Open Channels or Sewers

Methods available can be divided as follows:

1. Velocity methods
2. Level measurement methods
3. Miscellaneous techniques

2.4.3.1 Velocity Method - These techniques can be applied when the cross sectional area can be determined and when the flow variability is low.

1. Measurement with velocity indicating instruments.

   a. Current meters - To apply a current meter, use the following procedures (18, 19):

      1) Place meter facing upstream as close to vertical as possible.

      2) Take measurements at equal distances across the channel. Total flow is sum of the parts.

      3) Take single measurement at depth of approximately 60% below the surface. This method is used for shallow waters where the two point method is not applicable.

      4) Take double measurements at 20% and 80% below the surface and average. This technique is used for depths greater than two feet.

      5) Other methods include: six-tenths depth method, vertical velocity curve method, subsurface method, integration methods, three point type. For details see reference 16.

b. Pitot tube - Use the same equation as before. Take measurements at equa-distant points across a flow stream. It is difficult to obtain accurate measurements at low velocities with this equipment (17).

2. Measurement of time of passage

a. Dye injection - Add a water soluble dye or tracer to the water and measure the time from the instant it is dropped to the point of either maximum color intensity or highest measurable concentration (20). Materials commonly used are disodium fluoresein dye and lithium chloride salts. For more accuracy, several measurements should be taken and the results averaged.

b. Floats - Drop a float into the water and measure the time needed for it to travel a known distance. This establishes surface velocity which is multiplied by a coefficient of 0.85 to 0.95 depending on the depth of water, the velocity and the nature of the stream or canal bed (7). Therefore this coefficient is difficult to accurately establish and this float technique should be used only as a flow rate approximation.

2.4.3.2 Level Measurement Methods - Level measurement is a technique which allows the determination of flow by creating an obstruction and then measuring the height of backed up water. The primary devices, weirs and flumes create the obstruction and the secondary devices measure the water level.

1. Primary devices

a. Weirs - A weir is a dam over which the water flows. The most common type is a sharp crested weir of which there are three varieties: 1) rectangular, 2) Cipolletti and 3) triangular or V-notch.

The common form of the weir equation is:

$Q = C\ L\ H^{3/2}$ or weir velocity head correction

$$Q = CL\ (H+L)^{3/2} - h^{3/2}$$

h = velocity head in feet

Q = flow, cfs (cu m/sec = cfs x 0.0283)

L = effective width of the weir in ft

H = head, ft

C = coefficient dependent upon type of weir

where C = 3.33 rectangular
C = 3.367 Cipolletti
C = 2.49 for V notch weir

A typical sharp crested weir is shown in Figure 2.5.

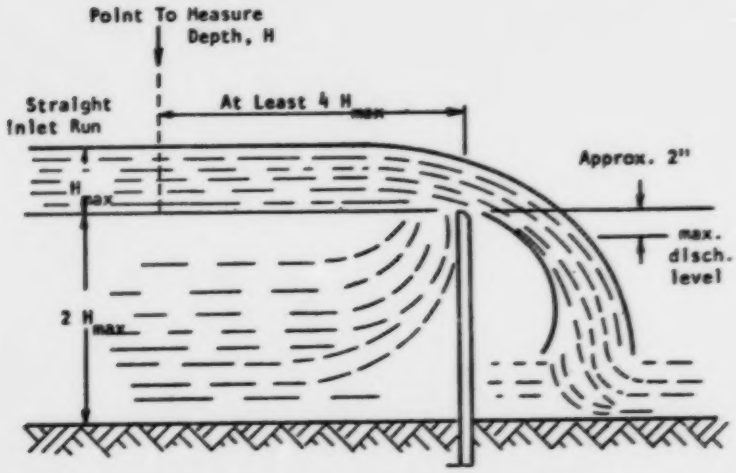


Figure 2.5 Sharp crested weir (12)

The approximate flow determines the type of weir to use. A rectangular weir should be used for flows greater than 2 cfs. V-notch weirs are used for flows of less than 1.0 cfs (1.7 cu m/min) and can be used in the range of 1.0 to 10.0 cfs (1.7 to 17 cu m/min) (20). The Cipolletti weir is accurate in the same range as the rectangular weir and is often used in irrigation ditches. The flow equation is modified by changes in the C value and L value by the different weirs. Nomographs for rectangular and triangular weirs are included to simplify application of these formulas. However, with the availability of hand calculators, the more accurate calculations should be used when possible (see Figure 2.6 and 2.7).

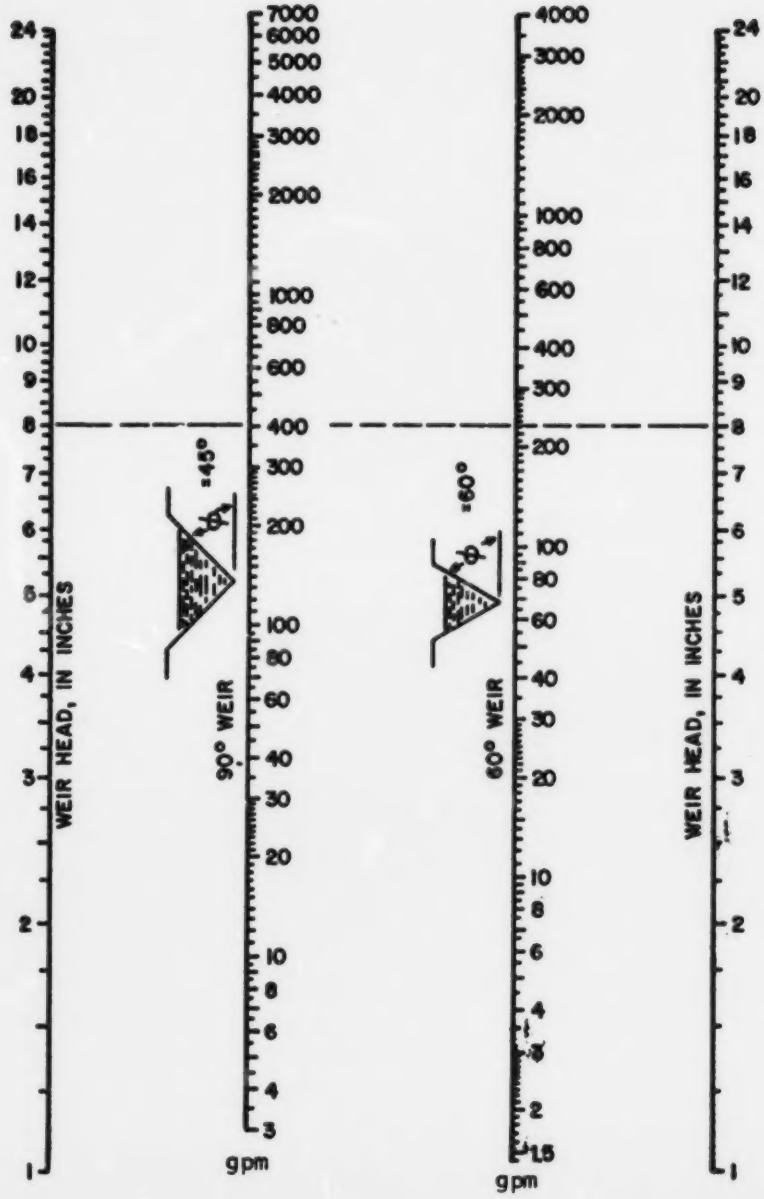
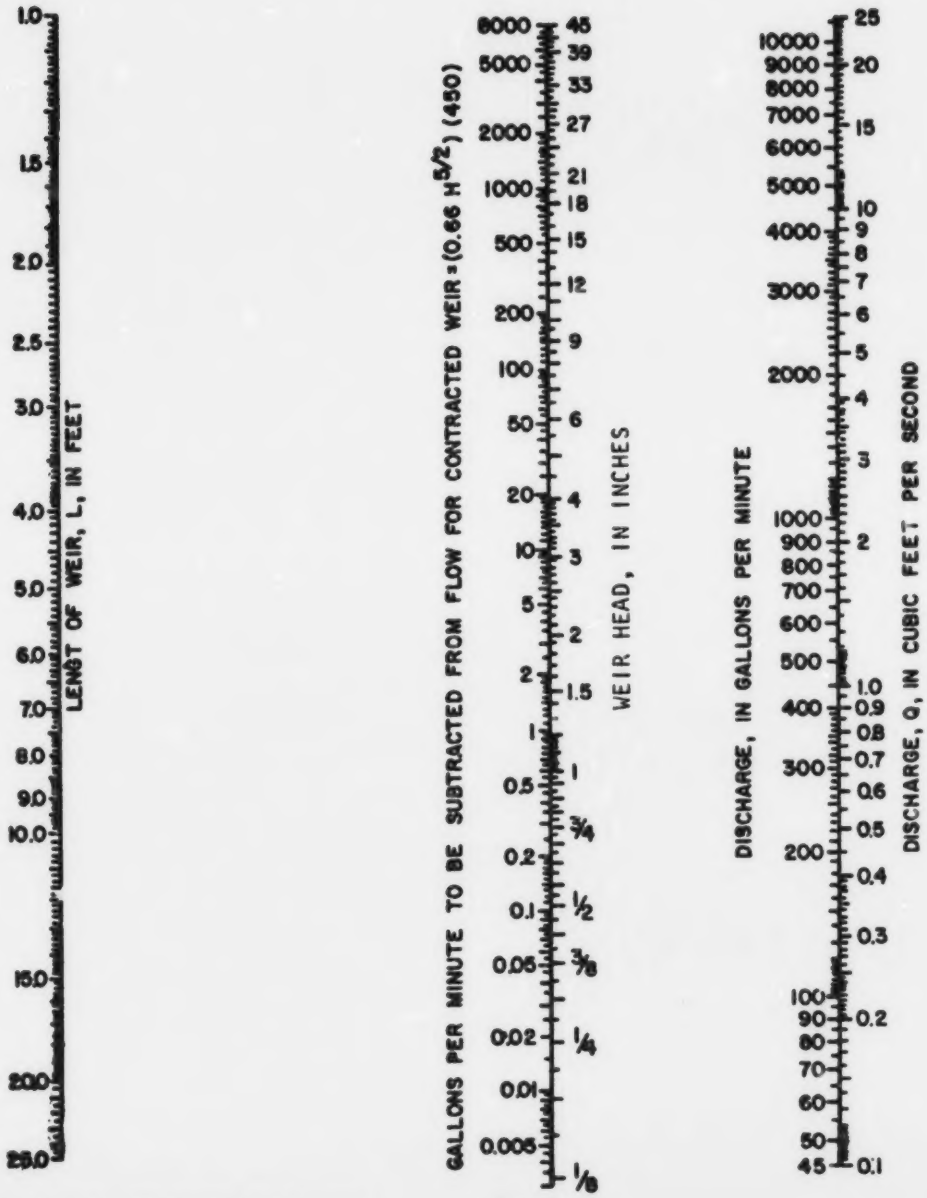


Figure 2.6. Flow rates in gallons per minute for 60° and 90° V-notch weirs (12)



Note: Based on Francis weir formula as follows:

$Q = 3.33\,LH^{3/2}$ (for suppressed weir)

or

$Q = 3.33\,(L - 0.2H)\,H^{3/2}$

$= 3.33\,LH^{3/2} - 0.66\,H^{5/2}$ (for contracted weir with two end contractions)

Where:

Q = discharge, in cubic feet per second.

L = length of weir, in feet.

H = head in feet.

Figure 2.7. Nomograph for capacity of rectangular weirs (12)

b. For installation of weirs, the following criteria should be met (20):

1) The upstream face of the bulkhead should be smooth and in a vertical plane perpendicular to the axis of the channel.

2) The upstream face of the weir plate should be smooth, straight, and flush with the upstream face of the bulkhead.

3) The entire crest should be a level, plane surface which forms a sharp, right-angled edge where it intersects the upstream face. The thickness of the crest, measured in the direction of flow, should be between 0.03 and 0.08 inch (about 1 to 2 mm). Both side edges of rectangular weirs should be truly vertical and of the same thickness as the crest.

4) The upstream corners of the notch must be sharp. They should be machined or filed perpendicular to the upstream face, free of burrs or scratches, and not smoothed off with abrasive cloth or paper. Knife edges should be avoided because they are difficult to maintain.

5) The downstream edges of the notch should be relieved by chamfering if the plate is thicker than the prescribed crest width. This chamfer should be at an angle of 45° or more to the surface of the crest.

6) The distance of the crest from the bottom of the approach channel (weir pool) should preferably be not less than twice the depth of water above the crest and in no case less than 1 foot.

7) The distance from the sides of the weir to the sides of approach channel should preferably be no less than twice the depth of water above the crest and never less than 1 foot.

8) The overflow sheet (nappe) should touch only the upstream edges of the crest and sides.

9) Air should circulate freely both under and on the sides of the nappe.

10) The measurement of head on the weir should be taken as the difference in elevation between the crest and the water surface at a point upstream from the weir a distance of four times the maximum head on the crest.

11) The cross-sectional area of the approach channel should be at least 8 times that of the overflow sheet at the crest for a distance upstream from 15 to 20 times the depth of the sheet.

12) If the weir pool is smaller than defined by the above criteria, the velocity of approach may be too high and the staff gage reading too low.

c. Flumes - Flumes are more expensive and more difficult to install than weirs but they allow the measurement of wide ranges of flows with little headloss.

1) Parshall Flume - This is commonly used to measure sewer flow using the following equation:

$$Q = 4W\,H^n$$

Q = discharge, cfs (cu m/sec = cfs x 0.0283)

W = throat width, ft

H = head of water above level flow

$$n = 1522\,W^{0.026}$$

A nomograph is included to simplify the calculation (Figure 2.8). Figure 2.9 shows a schematic of a Parshall flume.

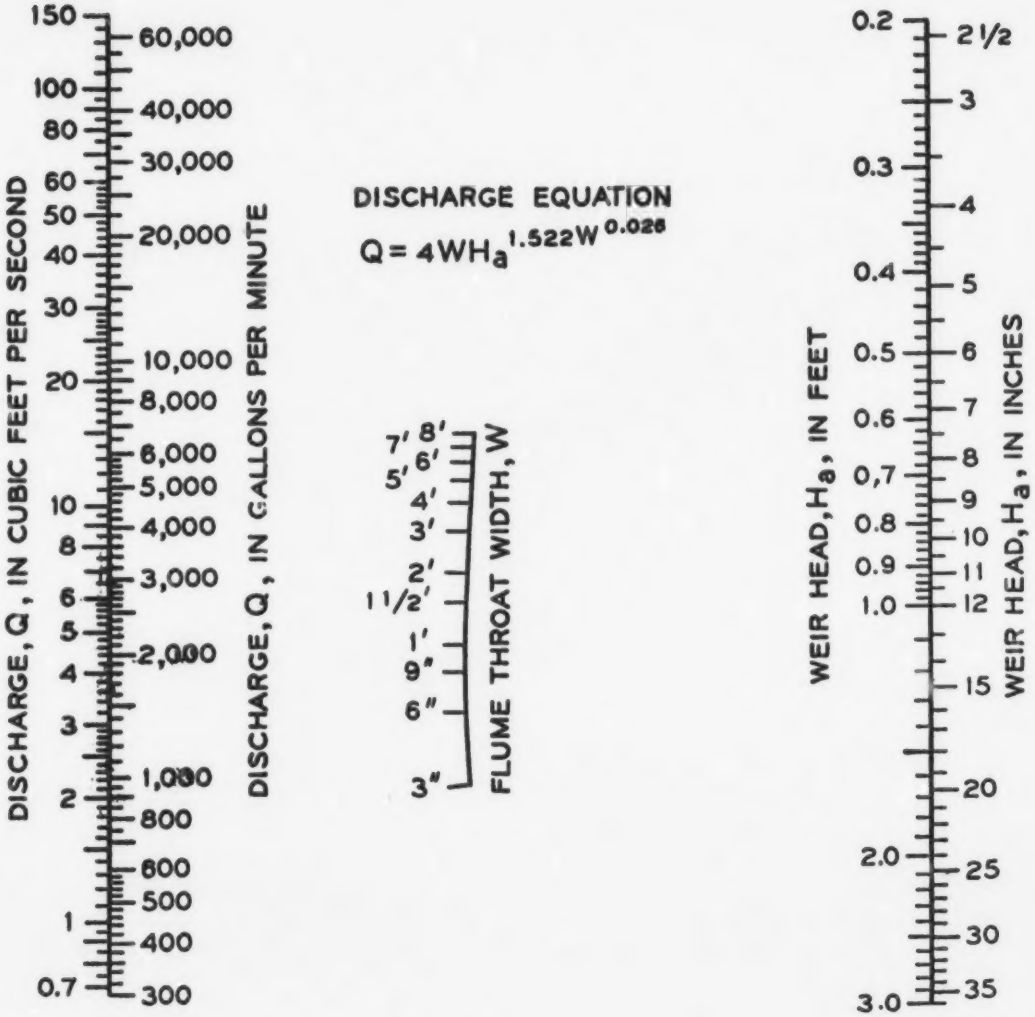


Figure 2.8. Nomograph to determine free flow through 3-in. to 8-ft. Parshall flumes (12)

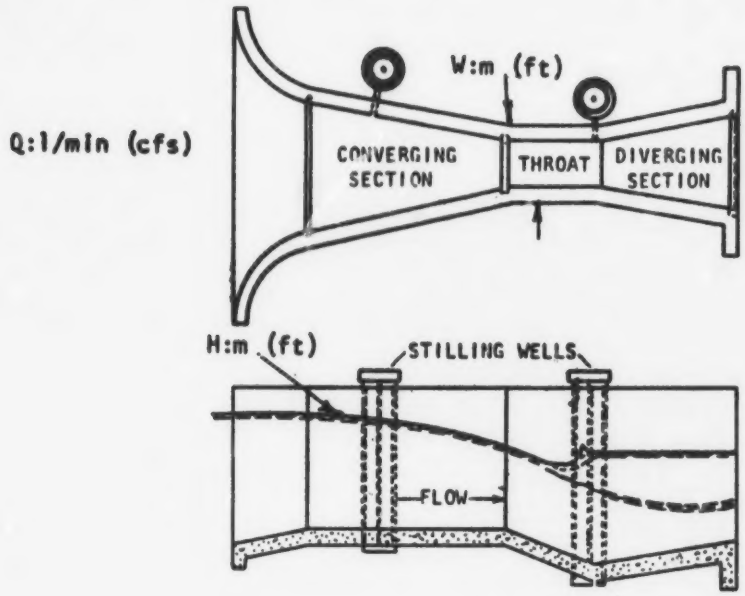


Figure 2.9. Parshall flume

2) Palmer-Bowlus Flumes - These flumes are shorter, fit flush with the bottom of a sewer and are more conveniently installed as fiberglass inserts. To calculate flow the following equation is used:

$$\frac{Q^2}{g} = \frac{A_c}{b} \qquad \frac{V_c^{\,2}}{2g} = \frac{A_c}{2b} = \frac{d_c}{2}$$

A_c = area at critical depth, m^2 (ft^2)

d_c = critical depth, m (ft)

V_c = critical velocity, m/sec (fps)

b = width of flume, m (ft)

Q = discharge, m^3/sec (cfs)

g = gravitational constant 9.8 m/sec^2 (32.2 ft/sec^2)

For installation of flumes, use the same procedures as used for installation of weirs.

d. Submergence - The effect of submergence is to cause large inaccuracies in the flow measurement. The submergence is defined as the ratio of backwater level to crest level. Weirs cannot be used when submerged, however, correction factors can be applied to flumes at submergence up to 70% (21).

2. Choice of primary device - The advantages and disadvantages or weirs and flumes are listed in Table 2.6. If feasible a flume is preferable because of the greater accuracy.

Table 2.6. ADVANTAGES AND DISADVANTAGES OF FLUMES AND WEIRS

Advantages	Disadvantages
Weirs:	
Inexpensive	Difficult to prevent leaks
Easily shop fabricated	High headloss created
Easily obtained	Must achieve free discharge, proper approach velocity, proper level to head ratio for accurate measurement Solids accumulation in front of weir
Flumes:	
Self-cleaning	Large size
Low headloss	Difficult to fit
Greater range of accuracy	High cost of flumes
Dual "piggy-back", flumes available to extend flow range	Difficult to shop fabricate

3. Secondary Devices - There are six types of devices which measure the head or liquid level upstream of the primary devices:

a. Hook or staff gauge
b. Differential pressure measurement
c. Surface float
d. Dipper (level sensing probe
e. Ultrasonic
f. Wire weight from overhead structures

4. Choice of secondary devices-Table 2.7 compares the advantages and disadvantages of the level measuring devices.

Table 2.7 ADVANTAGES AND DISADVANTAGES OF SECONDARY DEVIES

Device	Advantages	Disadvantages
Hook gauge or stage board	Common, accurate	Manual only, stilling well may be needed
Differential Pressure Measurement		
a. Pressure bulb	No compressed air source, can be directly linked to sampler	Can clog openings, expensive
b. Bubbler tube	Self-cleaning, less expensive; reliable	Need compressed air or other air source; can't stand much abuse
Surface float	Inexpensive, reliable	In-stream float catches debris
Dipper	Quite reliable, easy to operate	Oil and grease will foul probe, expensive, possible sensor loss
Ultrasonic	No electrical or mechanical contact	Air bubbles may cause echo rebounding

In addition to above considerations, the following must be considered:

1. Is flow-proportional sampling to be done?
2. Is a manual or automatic composite desired? (i.e., is the flow monitor separate or attached to the sampler)
3. Is a record of flow needed?

A summary of the advantages and disadvantages for both the primary and secondary types of devices is included in Table 2.8.

Table 2.8 RELATIVE COMPARISON OF PRIMARY AND SECONDARY OPEN CHANNEL FLOW MEASUREMENT DEVICES (a)

	Primary devices			Secondary devices				
Characteristic	Channel char's only (Manning formula	Weir	Flume	Hook gauge, stage board	Differential pressure	Float Device	Dipper	Ultra-sonic
Suitable for continuous measurement	+	+	+	-	+	+	+	+
Capability for sending signal to sample (flow-proportional sampling)	na	na	na	-	+	+	+	+
Need for stilling well	na	na	na	+	-	+	-	-
Low initial cost	3	2	1	3	2	3	1	1
Easy to install	na	2	1	3	2	1	2	2
Hight accuracy of measurement	1	2	3	2	3	3	3	3
Low maintenance (incl. cleaning)	3	1	3	3	2	2	3	3
Suitable for high solids wastewater	3	2	3	3	3	2	2	3
Low susceptibility to fouling (rags, debris, grease)	3	1	3	3	2	1	1	3
Wide flow range	3	2	3	+	+	+	+	+
Low headloss	3	1	3	+	+	+	+	+
Low auxiliary requirements (manpower, compressed air, AC power)	na	na	na	1	2	3	3	1

(a) na = not applicable
- = no or not suitable
+ = yes or suitable

1 = fair, frequently a problem
2 = good, sometimes a problem
3 = excellent, seldom or never a problem

2.4.3 Miscellaneous Flow Measurement

2.4.3.1 Friction Formula - Measurement of surface slope and channel velocity and depth can be used to roughly estimate flow (13). The Manning formula is commonly used for estimating a flow:

$$V = \frac{1.486}{n} R^{2/3} S^{1/2}$$

V = avg. velocity, fps (m/sec = fps x 0.3048)

n = coefficient of roughness

R = hydraulic radius, ft (= $\frac{\text{cross-sectional area}}{\text{wetted perimeter}}$)

S = slope of energy grade line

2.4.3.2 Tracer Techniques - Tracers of radioactive materials can be used in two ways: 1) Two Point Method, and 2) Total-Count Method. However, both techniques require an experienced operator, permits, and equipment not commonly available to sampling crews (12).

2.4.3.3 Salt Dilution Method - In this technique a known amount of salt is added to a stream and then the dilution is determined after it has traveled downstream (20).

$$Q = q \frac{C_1 - C_2}{C_2 - C_o}$$

Q = stream discharge

C_o = natural concentration instream

C_1 = tracer concentration

C_2 = final concentration

q = injection rate

2.4.3.4 Water Meters - An estimate of the flow can be obtained from water meter readings when an instantaneous flow rate is not critical. This technique is used in a confined area, such as the industrial plant. A material balance is made of the incoming and outgoing flow as a check or initial estimate of the flow rate (13).

2.4.3.5 Measuring Level Change in Tank - In some instances the level change in a tank can be used to estimate flow. To accomplish this, the volume of the tank as related to depth must be established; then the flow is allowed to enter and the level change with time recorded.

2.4.3.6 Pump Rates - When other methods are not available for flow measurement, and a pump is used in the system, the operating characteristics of the pump can be used to estimate flow. One method is to record the pumping time and the pump capacity at discharge pressure and then refer to manufacturers head curves for the total flow (25).

Another technique is to establish the pump's horsepower and determine the capacity from the manufacturers curves. However, these techniques should be used only for estimates of flows.

2.4.3.7 Calibrated Vessel - Another technique useful for free falling water is to capture a known volume of water over a recorded time interval. The flow rate is then established for a specific time. More than one measurement is necessary to allow accurate estimates.

2.4.4 Flow Recording Equipment Errors (Reference 7)

Sources of measurement error with recording equipment are common to both weirs and flumes and include:

1. Stilling well in wrong location with respect to weir or flume area.

2. Trash or debris in stilling well and conduit between flume and well plugged.

3. Float dirty, punctured, not vertical and rubbing against side of stilling well. Slack in float cable.

4. Wrong recorder multiplier and chart paper. Pen not inked and not giving responsive trace. Recorder does not zero. An error in calibration of 1.5 cm (0.6 in.) can cause an error in rate measurement ranging from several hundred percent at low depths on small weirs and twenty to thirty percent for moderate depths in flumes with throat widths under 30.5 cm (12 in.)

2.5 PRACTICAL FEATURES OF SAMPLING

Follow these procedures when collecting water samples (3, 22, 23, 24):

1. Obtain from the principal investigator written and specific instructions on sampling procedure.

2. Check all sampling equipment prior to use to ensure good operating conditions and cleanliness.

3. Check all sample bottles to avoid contamination.

4. Clean sampler intake tubing by flushing with hot water and then rinsing. If organic or other contamination remains, replace tubing and flush to remove organics. Clean bottles as indicated in 3.4. If this cannot be done, rinse at least twice with water to be sampled.

To obtain representative samples, follow these guidelines.

1. Take sample where wastewater is well mixed (e.g. near a Parshall flume or at a point of hydraulic turbulence such as downstream of a hydraulic jump). Weirs tend to enhance the settling of solids upstream and accumulate floating solids and oil downstream, therefore such locations should be avoided as a sample source. For low level turbulence, mechanical or air mixing should be used to induce turbulence except when dissolved gases or volatile materials are being sampled.

2. Take sample at 0.6 depth in a chanel or where velocity or mixing is sufficient to prevent solids deposition.

3. Place mouth of collecting container below the water surface to avoid an excess of floating material.

4. Do not include large nonhomogeneous particles in the sample (e.g. leaves in a surface water sample, rags in a municipal influent sample).

5. Collect sufficient volume to allow duplicate analyses and quality assurance testing (split or spiked samples). The basic required volume is a summation of that required for the parameters of interest as given in Chapter 10.

6. Maintain an up-to-date log book which notes possible interferences, environmental conditions and problem areas.

7. Follow additional guidelines for manual sampling:

    a. Sample facing upstream to avoid contamination.
    b. Force sampling vessel through the entire cross section of the stream whenever possible.
    c. Drop an inverted bucket and jerk line just before impact with the water surface.
    d. Be certain that the sampler closes at the proper time before sampling with a depth sampler. If a doubt exists, discard sample and resample.

8. Composite samples according to the converted flow rate as opposed to the raw measurement produced by the secondary device such as the head above a weir. The mathematical relationship between flow rate and the measurement produced by secondary devices are nonlinear functions and considerable error, especially for highly variable flows, will result from compositing samples based on the raw measurement (10).

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CHAPTER 3

GENERAL CONSIDERATIONS OF SAMPLE PRESERVATION AND HANDLING

Immediate analysis at the site of sampling will preclude the need for sample preservation; however, this procedure is not practical in most situations. Therefore, sample preservation and other related aspects of sample handling should be established to maintain the sample in its initial state until analysis. The following terms are used in this discussion:

1. Preservation Method (Technique) - special handling of the sample between time of sampling and analysis to maintain the integrity of constituents.

2. Preservative - chemical added to a sample to maintain integrity.

3. Holding Time - time between collection of the first sample portion and analysis.

Some aspects of sampling are not dependent upon analysis or water type. These are discussed in the following categories:

1. Universal Preservative
2. Sample Identification
3. Chain of Custody
4. Container Type and Cleaning
5. Holding Times
6. Volume of Sample

3.1 UNIVERSAL PRESERVATION

No single preservative has been found which maintains the integrity of all parameters in a sample.

3.1.1. Chemical Addition

The most convenient preservative is a chemical which can be added to a sample bottle prior to sampling and immediately disperses when the

sample is added, stabilizing all parameters for long periods of time. However, due to the biological nature of some tests (specifically BOD) and the fact that chemical composition can be affected by chemical addition (for example, adding nitric acid and analyzing for nitrate), there presently is no chemical available to preserve all parameters.

3.1.2 Freezing

Freezing has been the subject of many preservation studies (1-22). It is felt by some that freezing would be a method for increasing the holding time and allowing collection of a single sample for all analyses. However, the residue solids components (filtrable and nonfiltrable) of the sample change with freezing and thawing (23). Therefore, return to equilibrium and then high speed homogenization is necessary before any analysis can be run. This technique may be acceptable for certain analyses but not as a general preservation technique.

3.1.3 Refrigeration

Refrigeration (or icing) has also been studies with various results (10, 11, 13-15, 24-29). This is a common technique used in field work and has no detrimental effect on sample composition. Although it does not maintain complete integrity for all parameters, it does not interfere with any of the analytical methods.

3.2 SAMPLE IDENTIFICATION

3.2.1 Sample Number

Assign each sample container a unique number for identification in the field and laboratory. The identification number should have as few digits as possible to discourage abbreviation. The following guidelines should facilitate proper identification:

1. Use preprinted rolls of peel back labels assigned from the laboratory to a sampling crew.

2. For relatively small numbers of samples use sequential numbering and affix a label to each bottle. When the same sample is placed in two or more containers, assign two or more numbers to that sample. For large numbers of samples such as encountered in river, lake, or estuary sampling, use a five digit number, the first two numbers indicating the week of the year. When a sample is split into two or more parts, use one sample number and apply a color coded label to each sample which indicates the type of preservative added. Therefore, once the type of preservative has been indicated, the general group of parameters to be analyzed on that sample is established. For example, a blue

label indicates that nitric acid has been added, therefore, the analyst could obtain an aliquot from this sample for metal analysis.

3. Note the data and preservative on the label.

4. Note additional information in the field notebook.

3.3 CHAIN OF CUSTODY (30)

3.3.1 General

As in any other litigation, the Government must be able to demonstrate the reliability of its evidence in pollution cases by proving the chain of possession and custody of any samples which are offered for evidence or which form the basis of analytical test results introduced into evidence in any water pollution case. It is imperative that each EPA Regional Office and Laboratory prepare written procedures to be followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed. The primary objective of these procedures is to create an accurate written record which can be used to trace the possession of the sample from the moment of its collection through its introduction into evidence. A sample is in custody if it is:

1. In actual physical possession, or

2. In view, after being in physical possession, or

3. In physical possession and locked up so that no one could tamper with it.

Two procedures are included relative to the transfer of custody of samples (31): 1) the transfer of individual samples and 2) the bulk transfer of a group of samples. Both procedures will be discussed where appropriate in the following material. If not otherwise stated, the procedures are the same.

3.3.2 Rules for Sample Collection

1. Handle the samples as little as possible.

2. Obtain samples using the guidelines in this handbook.

3. Individual samples - Attach a Chain of Custody Record bottle tag (see Figure 3.1) used in the transfer of individual samples to the sample container at the time the sample is collected. The tag should contain information on sample number, date, time taken, source of sample (including type of sample and name of firm), analyses required, name of person taking sample and witnesses. The tag should be signed, time recorded and

(FRONT SIDE)

CHAIN OF CUSTODY RECORD

ENVIRONMENTAL PROTECTION AGENCY
National Field Investigations Center-Denver
Denver Federal Center
Denver, Colorado 80225

Sample No.	Time Taken (hrs)	Date Taken
Source of Sample		Preservative
Sample Collector	Witness(es)	
Remarks: (Analyses Requires, Sample Type, etc.)		

(BACK SIDE)

I hereby certify that I received this sample and disposed of it as noted below:

Receipt of Sample			
	Received from	Date Received	Time Received
	Disposition of Sample	Signature	

I hereby certify that I received this sample and disposed of it as noted below:

Receipt of Sample			
	Received from	Date Received	Time Received
	Disposition of Sample	Signature	

I hereby certify that I obtained this sample and dispatched it as shown below:

Dispatch of Sample			
	Date Obtained	Time Obtained	Source
	Date Dispatched	Time Dispatched	Method of Shipment
	Sent to	Signature	

Figure 3.1 Chain of custody record tag

dated by the person taking the sample. The sample container may then be sealed with a preprinted, gummed seal containing the Agency's designation, date and signature of the person taking the sample (see Figure 3.2). The seal should cover the string or wire tie of the Chain of Custody bottle tag so that the tag cannot be removed and the container cannot be opened without breaking the seal. The tags and seals must be filled out legibly in ballpoint (waterproof ink).

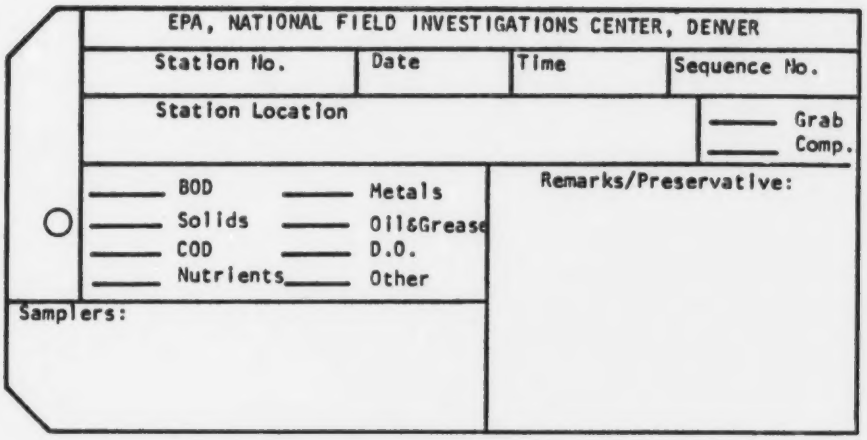
U.S. ENVIRONMENTAL PROTECTION AGENCY	SAMPLE No.	SEAL BROKEN BY	DATE
	SIGNATURE		
	PRINT NAME and TITLE (INSPECTOR, ANALYST, TECHNICIAN etc.)		

Figure 3.2. Gummed seal for sample bottles

Bulk or Group Samples - Attach a sample tag as shown in Figure 3.3 to the sample bottle. The gummed label seal is no longer necessary. Sample transfer is accomplished in groups using a group sample chain of custody record as described later (Figure 3.6).

4. Record field measurements and other pertinent information in a bound field notebook or log. Sufficient information must be included to refresh the memory of sampling personnel in the event that a witness is required at an enforcement proceeding. A separate set of field notebooks should be maintained for each survey and stored in a safe place where they can be protected and accounted for at all times. Establish a field data record format to minimize field entries or possible omissions. The following information should be included:

date	field measurements
time	such as:
survey name	temperature
type of samples taken	conductivity
volume of each sample	DO
type of analyses	pH
sample numbers	flow
sample location	other pertinent information



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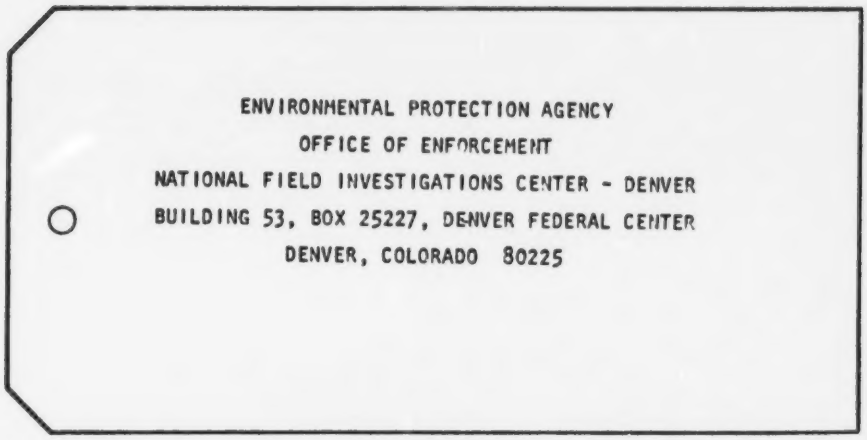

BACK

Figure 3.3 Bottle sample tag used by NFIC - Denver (31)

The entries should be signed by the person taking the sample and errors crossed out with one line and initialed. Assign a survey coordinator or designated representative the responsibility for preparing and retaining field notebooks during and after the survey (see Figure 3.4).

5. Watch the sample carefully during the time it is collected and dispatched to a receiving laboratory or turned over to an assigned custodian. The person taking the sample is responsible for the care and custody of the sample and must assure that each container is in his physical possession or view at all times or is stored in a locked place where no one can tamper with it.

6. Take color slides or photographs of the outfall sample location and any visible water pollution. Document in writing on the back of the photo the following information: signature of the photographer, time, date and site location. Photographs of this nature, which may be used as evidence, should be handled according to the established Chain of Custody procedures to prevent alteration.

3.3.3 Transfer of Custody and Shipment

The following procedures should be followed when samples are transferred or shipped.

1. a. Individual Samples

When transferring possession of individual samples, the transferree must sign and record the date and time on the Chain of Custody Record Tag (see Figure 3.1). Record custody samples for each individual sample when transfers are made to a field sample custodian. To reduce the number of custody cards, reduce the number of custodians in the chain of possession.

b. Bulk or Group Samples

When transferring possession of a group of samples, the Chain of Custody Record Form (see Figure 3.5) is used that allows the transfer of custody of the samples to the laboratory in groups. The transfer of custody of individual samples by signing bottle tags is not used. If a portion of the samples identified on the record form is to be transferred, the

Samplers: _____

FIELD DATA RECORD

STATION	SAMPLE NUMBER	DATE OF COLLECTION	TIME (HRS.)		pH	TEMPERATURE	OTHER PARAMETERS		
			SAMPLE TAKEN	SAMPLE RECEIVED BY LAB					

Figure 3.4 An example of a field log sheet

SURVEY				SAMPLERS: (Signature)					
STATION NUMBER	STATION LOCATION	DATE	TIME	SAMPLE TYPE Water Comp	Water Grab	Air	SEQ. NO	NO OF CONTAINERS	ANALYSIS REQUIRED

Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Relinquished by: (Signature)	Received by Mobile Laboratory for field analysis: (Signature)	Date/Time
Dispatched by: (Signature) Date/Time	Received for Laboratory by:	Date/Time
Method of Shipment:		

Distribution: Orig. – Accompany Shipment
1 Copy – Survey Coordinator Field Files

Figure 3.5. Chain of custody record form

individual samples are noted in the column with the signature of the person relinquishing them. The field laboratory person receiving the samples acknowledges receipt by signing in the appropriate column.

2. The field custodian or person taking the sample, if a custodian has not been assigned, is responsible for properly packaging and dispatching samples to the appropriate laboratory for analysis. This responsibility includes properly filling out, dating and signing the "dispatch of sample" portion of the Chain of Custody Record tag (See Figure 3.1) used for single sample transfer.

3. Package samples properly to avoid breakage. The shipping containers should be padlocked for shipment to the receiving laboratory. Preprinted gummed seals may be utilized to seal the package so that tampering can be detected (see Figure 3.2).

4. In the case of the transfer of individual samples, all packages should be accompanied by a Sample Transmittal Form identifying the contents (see Figure 3.6). The original of the completed form and one copy should accompany the shipment, one copy should be delivered directly to the laboratory and to data management, and a copy should be retained by the survey coordinator. When bulk transfer of a group of samples is used, all packages should be accompanied by the Chain of Custody Record (see Figure 3.5) showing identification of the contents.

5. If samples are delivered to the laboratory when appropriate personnel are not there to receive them, the samples must be locked in a designated area within the laboratory so that no one can tamper with them. The person who received and locked the samples must be the one who later delivers custody to the appropriate custodian.

3.3.4 Laboratory Custody Procedures

Chain of Custody procedures are also necessary in the laboratory from the time of sample receipt to the time it is discarded. The following procedures should be used in the laboratory.

TO: (Laboratory Name and Address)

FROM: (Field Custodian or Field Sampler)

Sample No.	Lab Number	Method Of Preservation	Analysis Required
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

To be completed in Field:

Prepared by: _____ Date: _____

(Signature)

Field Notebook No. _____ Time: _____

To be Completed by Laboratory:

Received by: _____ Date: _____

(Signature)

Time: _____

Distribution: Original & 1 copy - Accompany shipment
1 copy - Mail Directly to Laboratory
1 copy - Mail to Data Management
1 copy - Survey Coordinator Field Files

Figure 3.6 Sample Transmittal Form

1. The laboratory should designate two full-time employees: one as a sample custodian and the second as an alternate. In addition, the laboratory should designate a clean, dry, isolated room that can be securely locked from the outside as a "Sample Storage Security Area". The sample custodian must maintain a permanent log book in which he records, for each sample, date and time received, source of sample, sample number, how transmitted to laboratory, and the number assigned to each sample by the laboratory. A standardized format should be established for log book entries.

2. Samples should be handled by the minimum possible number of persons.

3. In the case of the transfer of individual samples, all the incoming samples should be received only by the custodian, who shall indicate receipt by signing the accompanying Sample Transmittal Form (see Figure 3.6) and who shall retain the signed forms as permanent records. When bulk transfer of a group of samples is used, the custodian should sign the Chain of Custody Record sheet (see Figure 3.5), and also retain the sheet as a permanent record.

4. Immediately upon receipt, the custodian should affix a number to the attached tag, record the required information in the log book and preserve the sample according to the recommendations in Chapter 10 if this has not been done already. Store the sample in a locked sample room. This room should be unlocked only when the analyst removes or replaces samples.

5. The custodian only should distribute samples to appropriate laboratory personnel performing analyses. The custodian should enter in the log the laboratory sample number, time, and date and the signature of the person to whom the samples were given.

6. If a gummed label seal was used on the individual sample container, laboratory personnel should examine the seal on the container prior to opening. They should be prepared to testify that their examination of the sample container indicated that it had not been tampered with or opened.

7. The analyst must record in his log book the name of the person from whom the sample was received, whether it was sealed, identifying information describing the sample (by origin and sample identification number), the procedures performed and the results of the testing. He should sign and date his notes and retain them as a permanent laboratory record. Laboratory personnel should be prepared to justify any deviations from standard procedures during cross-examination. In the event that the person who performed the tests is not available as a live witness at the time of trial, the government may be able to introduce the notes in evidence under the Federal Business Records Act or the Federal Rules of Evidence law.

8. Laboratory personnel are responsible for the care and custody of the sample once it is handed over to them and should be prepared to testify that the sample was in their possession and view or securely locked up at all times from the moment it was received from the custodian until the tests were run.

9. Once the sample testing is completed, the unused portion of the sample, together with all identifying tags and seals, should be returned to the custodian who will make appropriate entries in his log. The returned tagged sample should be retained in the sample room until it is required for trial. Other testing documentation also should be turned over to the custodian.

10. Samples, tags, and laboratory records of tests should be destroyed only upon the order of the laboratory director, in consultation with previously designated regulatory officials.

3.4 CONTAINER TYPE AND CLEANING

A variety of factors affect the choice of containers and cap material. These include resistance to breakage, size, weight, interference with constituents, cost and availability. There are also various procedures for cleaning and preparing bottles depending upon the analyses to be performed on the sample.

3.4.1 Container Material

The two major types of container materials are plastic and glass (32).

Glass:

1. Kimax or Pyrex brand (borosilicate)
2. Vycor
3. Corning
4. Ray-Sorbor Low-Actinic
5. Corex

Plastic:

1. Conventional polyethylene
2. Linear polyethylene
3. Polypropylene
4. Polycarbonate
5. Rigid polyvinyl chloride
6. Teflon

All these materials have various advantages and disadvantages. Kimax or Pyrex brand borosilicate glass is inert to most materials and is recommended where glass containers are used. Conventional polyethylene is to be used when plastic is acceptable because of reasonable cost and less adsorption of metal ions (33). The specific situation will determine the use of glass or plastic. However, use glass containers if pesticides or oil and grease are to be analyzed. Table 3.1 summarizes the advantages and disadvantages of these materials.

Table 3.1. COMPARISON OF GLASS AND PLASTIC CONTAINERS

	Borosilicate Glass	Conventional Polyethylene
Interference with sample	Inert to all constituents except strong alkali	All constituents except pesticides and oil and grease
Weight	Heavy	Light
Resistance to breakage	Very fragile	Durable
Cleaning	Easy to clean	Some difficulty in removing adsorbed components
Sterilizable	Yes	In some instances
Space	Takes up considerable space	Substantial space savings during extended field studies

3.4.2 Container Caps

There are two main types of plastic container caps: polyethylene and bakelite with liners. Use polyethylene caps (ease of cleaning) except if these caps do not fit tightly to the container or if pesticides or oil and grease analyses are to be performed. Teflon liners should be used for pesticides and oil and grease samples. There are three liner types available and the advantages/disadvantages are listed in Table 3.2.

Table 3.2 COMPARISON OF CAP LINERS

Liner Type	Advantages	Disadvantages
Wax coated paper	Generally applicable to all samples Inexpensive	Must be inspected prior to each use because of deterioration Cannot use with organics
Neoprene	Same as wax coated paper	Same as wax coated paper
Teflon	Applicable for all analyses Minimizes container/sample interaction Mandatory for pesticide analyses	High Cost.

3.4.3 Container Structure

Use a wide mouth container in most instances. This structure will permit easy sample removal. It is also easily cleaned, quickly dried, and can be stored inverted. Use a narrow neck bottle when interaction with the cap liner or outside environment is to be minimized. Use a cleaned solvent container for pesticide sample collection (34).

3.4.4 Disposable Containers

Use disposable containers when the cost of cleaning is high. These containers should be precleaned and sterile. The most commonly used disposable container of this type is the molded polyethylene cubitainer[R]

shipped nested and sterile to the buyer. However, since their cubic shape and flexible sides make them almost impossible to thoroughly clean, use these containers only once.

3.4.5 Container Washing

The following procedure should be followed to wash containers and caps:

1. Wash containers and caps with a non-phosphate detergent and scrub strongly with a brush (if possible wash liners and caps separately).

2. Rinse with tap water, then distilled water.

3. Invert to drain dry.

4. Visually inspect for any contamination prior to storage.

5. If the container requires additional cleaning, rinse with a chromic acid solution (35 ml of saturated sodium dichromate solution in 1 liter of sulfuric acid - this solution can be reused). Then rinse with tap water and distilled water and dry as indicated above.

3.4.6 Container Preparation

For certain parameters, a special cleaning procedure is needed to avoid adsorption or contamination due to interaction with container walls. These procedures are outlined below.

1. Acid Rinse: If metals are to be analyzed, rinse the container with a solution of one part nitric acid to four parts water then with distilled water. If phosphorus is to be analyzed, rinse the container with a solution of one part hydrochloric acid to one part water followed by distilled water.

2. Solvent Rinse: If oil and grease or pesticides are to be analyzed, rinse the sample container with hexane, then acetone, and distilled water. The container should have been previously cleaned with chromic acid solution as described in Section 3.4.5. Treat the container caps similarly.

3. Sterilization: For microbiological analyses, sterilize the container and its stopper/cap by autoclaving at 121 C for 15 minutes or by dry heat at 180 C for two hours. Heat-sensitive plastic bottles may be sterilized with ethylene oxide at low temperatures. Wrap bottles in kraft paper or cover with aluminum foil before sterilization to protect against contamination. See Standard Methods for details (33). An acceptable alternative for emergency or field use is sterilization of containers by boiling in water for 15 minutes.

3.5 HOLDING TIME

Holding times are specific to the analysis. However, when a series of analyses are to be done on the same sample, the parameters with the shortest holding time are to be analyzed first followed by the relatively stable parameters.

3.6 VOLUME OF SAMPLE

The volume of sample is dependent on the type and number of parameters, the type of instrumentation used for analyses (e.g. Technicon autoanalyzer), and expected concentrations of parameters in the wastewater. To determine the total sample volume, list all the parameters to be analyzed and the required volume as given in Chapter 10. Add the individual volumes to obtain the total sample volume required, then additional volumes as needed for split samples or for analytical quality control. It must be remembered that for many parameters required volumes of relatively clean surface water are greater than those of most wastewaters.

A minimum one liter sample is recommended when grab samples are analyzed and 3.785 L (1 gal.) is necessary if more than one analysis is to be performed on a single sample. An air space at the top of the container is recommended so the sample can be well mixed before aliquots are removed.

The minimum volume of discrete samples intended for later compositing is 400 ml (0.11 gal.). The final makeup volume of the composite should be approximately 3.8 L (1 gal.).

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CHAPTER 4

STATISTICAL APPROACH TO SAMPLING

For every sampling program four factors must be established:

1. Number of samples
2. Sampling frequency
3. Parameters to be measured
4. Location(s) of sampling

These variables are usually established in varying degrees by the discharge permit requirements which may or may not be scientifically sound. In those cases where a new program is being initiated or where the permit requirements need review, statistical methods and scientific judgment should be used to establish the best procedures.

4.1 BASIC STATISTICS AND STATISTICAL RELATIONSHIPS

Data representing a physical phenomenon are broadly classified as continuous or discrete and deterministic (those described by an explicit mathematical relationship or formula) or nondeterministic (random). Due to the nature of water quality changes and the complexity of the processes affecting the water or wastewater characteristics, there is no way to predict an exact value for a datum at a future instant in time. Such data are random in character and are conveniently described in terms of probability statements and statistical averages rather than by explicit equations. However, long-term changes in water quality tend to have a functional character with random fluctuation components. Statistical evaluation techniques provide a tool to detect and quantify both the deterministic (functional) and the nondeterministic (random) components of a water or wastewater quality record. Figure 4.1 shows the components of the record.

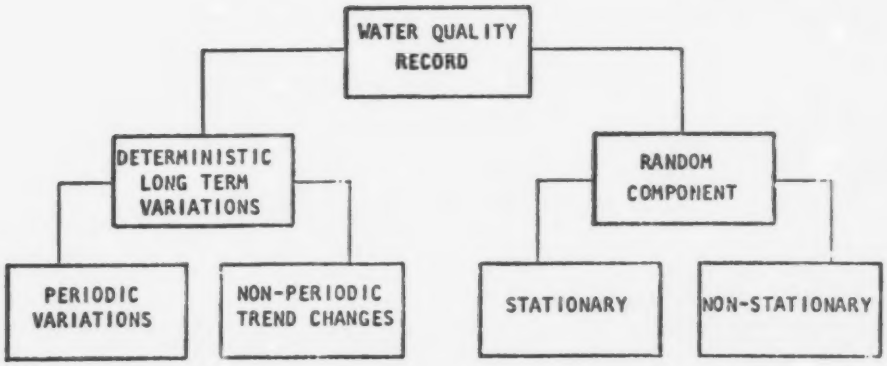


Figure 4.1 Statistical components of a water quality record

4.1.1 Statistical Parameters - Definitions

4.1.1.1 Mean - The average of all values X, on a time record.

continuous distribution (population or true mean):

$$\mu_x = \frac{1}{T} \int_0^T X(t)\, dt$$

discrete distribution (sample mean):

$$\bar{X} = \frac{1}{N} \sum_{i=1}^{N} X_i$$

i = subscript denoting location of the variables X on the record

$\bar{X}$ = estimation of the mean

N = number of discrete samples

T = time length of record

μ_x = true mean

t = time

4.1.1.2 Variance - A measure of the spread of the data about the mean $\bar{X}$.

continuous distribution (population or true variance):

$$\sigma_x^2 = \frac{1}{T} \int_0^T (X(t) - \bar{X})^2 \, dt$$

discrete distribution (sample variance):

$$S_X^2 = \frac{1}{N-1} \sum_{i=1}^{N} (X_i - \bar{X})^2 = \frac{1}{N-1} \left(\sum_{i}^{N} (X_i^2) - \frac{1}{N} \left(\sum_{i}^{N} X_i \right)^2 \right)$$

4.1.1.3 Standard Deviation - The square root of the variance having the same dimension as the variable X. Therefore, it is more convenient to express the spread of data by the standard deviation than by the variance.

$\sigma_x = \sqrt{\sigma_x^2}$ - population or true standard deviation

$S_X = \sqrt{S_X^2}$ - sample standard deviation

4.1.1.4 Variance of the Mean - The characteristic which describes the error of the estimate of the mean since the estimate will vary from the true or population mean due to a limited number of data points.

$$S_{\bar{X}}^2 = \frac{S_X^2}{N}$$

4.1.1.5 Standard Deviation of the Mean - Another expression of the error of the estimate of the mean; the square root of the variance of the mean.

$$S_{\bar{X}} = \frac{S_X}{\sqrt{N}}$$

4.1.1.6 Relative Error of the Standard Deviation - The relative range or difference between the upper and lower limits of the confidence interval of the standard deviation.

$$\frac{\Omega}{S_X} = \sqrt{N-1} \quad \sqrt{\frac{1}{\chi^2_{N-1;\ 1-\alpha/2}}} - \sqrt{\frac{1}{\chi^2_{N-1;\ \alpha/2}}}$$

Ω = range of difference between the upper and lower limits of the confidence interval of the standard deviation

χ^2 = chi-square statistic = $\frac{N_s^2}{\sigma^2}$

α = level of significance

4.1.1.7 Spectral Analysis - A technique for analyzing the recurrence intervals of variance in an existing data record. The power spectrum is plotted versus frequency to reveal all significant harmonic and random variations in the signal.

$$\Gamma x\ (f) = \text{power spectrum function} = \int_{-\infty}^{\infty} R_x(u) \exp\ (-j2\pi fu)\ du$$

$$R_x\ (u) = \text{autocovariance function} = \frac{1}{T}\int_0^T x\ (t) \cdot (tfu)\ du$$

where μ = lag time f = frequency

t = time $j = \sqrt{-1}$

T = time length of the record

4.1.1.8 Nyquist Frequency - A rule which states that the frequency of sampling should be at least twice the highest or maximum frequency

$$f_{sampling} \geq 2 f_{max}$$

Example: A data record shows a maximum 24-hour frequency of variation. Then, the sampling frequency should be at least 2 times the 24 hour dominant frequency, or at least once every 12 hours.

4.1.1.9 Coefficient of Variation - The coefficient of variation provides a relative measure of the variation or dispersion of a distribution.

$$\text{Coefficient of variation} = CV = \frac{S_x}{\bar{X}}$$

4.1.1.10 Coefficient of Skewness - The coefficient of skewness provides a relative measure of the degree of asymmetry of a distribution.

$$\text{Coefficient of skewness} = \frac{N\Sigma(X_i-\bar{X})^3}{(N-1)\ (N-2)\ S_x^3}$$

4.1.2 Probability Density Functions (1)

4.1.2.1 Gaussian or Normal Distribution - The most widely used distribution for describing the variability of sample values, x_i, around the mean, $\bar{X}$.

$$\text{Prob}\ [X(t) < X] = \int_{-\infty}^{X} \frac{1}{\sigma_x\sqrt{2\pi}} \exp\left[-\frac{(X-\mu_x)^2}{2\sigma_x^2}\right] dx = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Z} \exp-\frac{Z^2}{2}\ dZ$$

$$\text{where } Z = \frac{X - \mu_x}{\sigma_x}$$

These values are tabulated in Table 4.1. For this distribution, 68.3% of all values will be within the interval $\bar{X} \pm 1S_x$, 95.4% within the interval $\bar{X} \pm 2S_x$ and 99.7% within the interval $\bar{X} \pm 3S_x$ as Figure 4.2 shows.

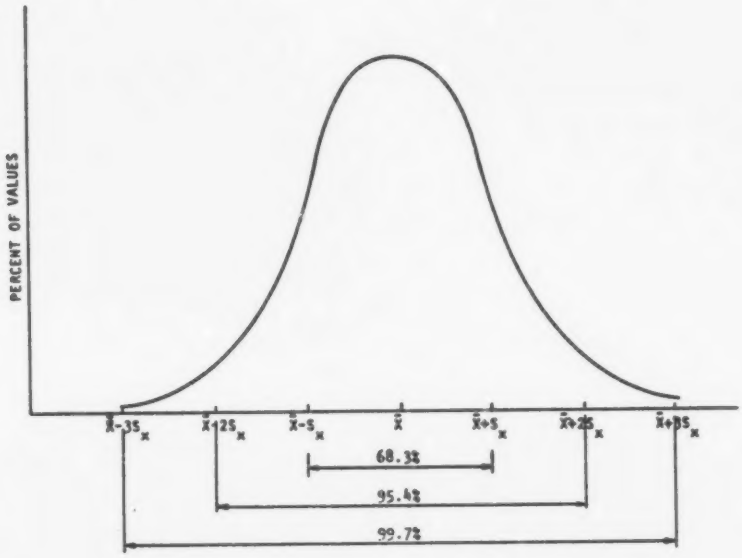


Figure 4.2. Gaussian or normal distribution

It can be seen that this distribution is defined from $-\infty$ to $+\infty$, therefore:

$$\text{Prob } [x(t) \leq X] = 1.0 - \text{Prob } [x(t) > X]$$

<u>4.1.2.2 Pearson Type III Probability Distribution</u> - This distribution is defined from 0 to $+\infty$ and is therefore applicable to water quality situations, since negative values do not exist.

$$\text{Prob } [x(t) \leq X] = \int_0^X Y_o \exp [-\gamma x] \cdot [1 + \frac{x}{d}]^{\gamma d} dx$$

Y_o, γ = coefficients

d = distance between mode and origin as shown in Figure 4.3

Table 4.1. AREAS UNDER STANDARDIZED NORMAL DENSITY FUNCTION (2)

$$\text{Value of } \alpha = \int_{x_\alpha}^{\infty} \frac{1}{\sqrt{2\pi}} e^{-x^2/2} = \text{Prob}[x > x_\alpha]$$

x_α	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.5000	0.4960	0.4920	0.4880	0.4840	0.4801	0.4761	0.4721	0.4681	0.4641
0.1	0.4602	0.4562	0.4522	0.4483	0.4443	0.4404	0.4364	0.4325	0.4286	0.4247
0.2	0.4207	0.4168	0.4129	0.4090	0.4052	0.4013	0.3974	0.3936	0.3897	0.3859
0.3	0.3821	0.3783	0.3745	0.3707	0.3669	0.3632	0.3594	0.3557	0.3520	0.3483
0.4	0.3446	0.3409	0.3372	0.3336	0.3300	0.3264	0.3228	0.3192	0.3156	0.3121
0.5	0.3085	0.3050	0.3015	0.2981	0.2946	0.2912	0.2877	0.2843	0.2810	0.2776
0.6	0.2743	0.2709	0.2676	0.2643	0.2611	0.2578	0.2546	0.2514	0.2483	0.2451
0.7	0.2420	0.2389	0.2358	0.2327	0.2296	0.2266	0.2236	0.2206	0.2177	0.2148
0.8	0.2119	0.2090	0.2061	0.2033	0.2005	0.1977	0.1949	0.1922	0.1894	0.1867
0.9	0.1841	0.1814	0.1788	0.1762	0.1736	0.1711	0.1685	0.1660	0.1635	0.1611
1.0	0.1587	0.1562	0.1539	0.1515	0.1492	0.1469	0.1446	0.1423	0.1401	0.1379
1.1	0.1357	0.1335	0.1314	0.1292	0.1271	0.1251	0.1230	0.1210	0.1190	0.1170
1.2	0.1151	0.1131	0.1112	0.1093	0.1075	0.1056	0.1038	0.1020	0.1003	0.0985
1.3	0.0968	0.0951	0.0934	0.0918	0.0901	0.0885	0.0869	0.0853	0.0838	0.0823
1.4	0.0808	0.0793	0.0778	0.0764	0.0749	0.0735	0.0721	0.0708	0.0694	0.0681
1.5	0.0668	0.0655	0.0643	0.0630	0.0618	0.0606	0.0594	0.0582	0.0571	0.0559
1.6	0.0548	0.0537	0.0526	0.0516	0.0505	0.0495	0.0485	0.0475	0.0465	0.0455
1.7	0.0446	0.0436	0.0427	0.0418	0.0409	0.0401	0.0392	0.0384	0.0375	0.0367
1.8	0.0359	0.0351	0.0344	0.0336	0.0329	0.0322	0.0314	0.0307	0.0301	0.0294
1.9	0.0287	0.0281	0.0274	0.0268	0.0262	0.0256	0.0250	0.0244	0.0239	0.0233
2.0	0.0228	0.0222	0.0217	0.0212	0.0207	0.0202	0.0197	0.0192	0.0188	0.0183
2.1	0.0179	0.0174	0.0170	0.0166	0.0162	0.0158	0.0154	0.0150	0.0146	0.0143
2.2	0.0139	0.0136	0.0132	0.0129	0.0125	0.0122	0.0119	0.0116	0.0113	0.0110
2.3	0.0107	0.0104	0.0102	0.00990	0.00964	0.00939	0.00914	0.00889	0.00866	0.00842
2.4	0.00820	0.00798	0.00776	0.00755	0.00734	0.00714	0.00695	0.00676	0.00657	0.00639
2.5	0.00621	0.00604	0.00587	0.00570	0.00554	0.00539	0.00523	0.00508	0.00494	0.00480
2.6	0.00466	0.00453	0.00440	0.00427	0.00415	0.00402	0.00391	0.00379	0.00368	0.00357
2.7	0.00347	0.00336	0.00326	0.00317	0.00307	0.00298	0.00289	0.00280	0.00272	0.00264
2.8	0.00256	0.00248	0.00240	0.00233	0.00226	0.00219	0.00212	0.00205	0.00199	0.00193
2.9	0.00187	0.00181	0.00175	0.00169	0.00164	0.00159	0.00154	0.00149	0.00144	0.00139

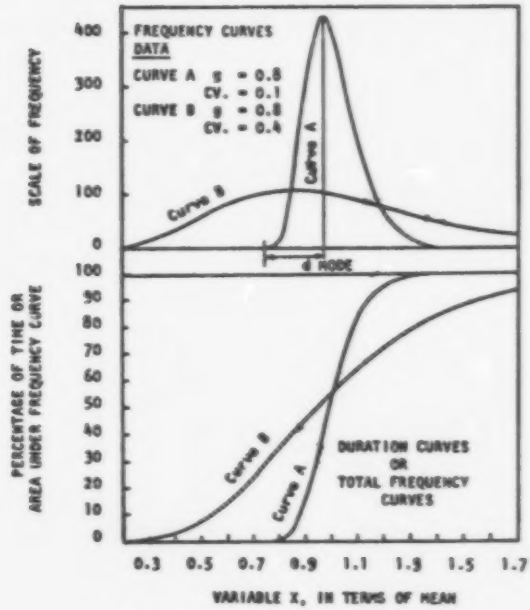


Figure 4.3. Pearson Type III probability distribution and density

4.1.2.3 Logarithmic Distributions - In certain situations, log-normal or log-Pearson Type III Distributions, where logarithms of the value X_i are evaluated instead of the arithmetic values, may give a better data fit.

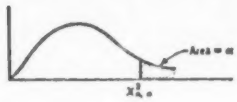
4.1.2.4 Chi Square Distribution - This function is the probability distribution of a random variable:

$$X_n^2 = Z_1^2 + Z_2^2 + Z_3^2 + \ldots + Z_n^2$$

$Z_1, Z_2, Z_3 \ldots Z_n$ = a series of n independent random variables each of which has a normal distribution with zero mean and unit variance. The values of the function is tabulated in Table 4.2.

Table 4.2. PERCENTAGE POINTS OF CHI-SQUARE DISTRIBUTION (2)

Value of $\chi^2_{n,\alpha}$ such that $\text{Prob}[\chi_n^2 > \chi^2_{n,\alpha}] = \alpha$



	α									
n	0.995	0.990	0.975	0.950	0.900	0.10	0.05	0.025	0.010	0.005
1	0.000039	0.00016	0.00098	0.0039	0.0158	2.71	3.84	5.02	6.63	7.88
2	0.0100	0.0201	0.0506	0.103	0.211	4.61	5.99	7.38	9.21	10.60
3	0.0717	0.115	0.216	0.352	0.584	6.25	7.81	9.35	11.34	12.84
4	0.207	0.297	0.484	0.711	1.06	7.78	9.49	11.14	13.28	14.86
5	0.412	0.554	0.831	1.15	1.61	9.24	11.07	12.83	15.09	16.75
6	0.676	0.872	1.24	1.64	2.20	10.64	12.59	14.45	16.81	18.55
7	0.989	1.24	1.69	2.17	2.83	12.02	14.07	16.01	18.48	20.28
8	1.34	1.65	2.18	2.73	3.49	13.36	15.51	17.53	20.09	21.96
9	1.73	2.09	2.70	3.33	4.17	14.68	16.92	19.02	21.67	23.59
10	2.16	2.56	3.25	3.94	4.87	15.99	18.31	20.48	23.21	25.19
11	2.60	3.05	3.82	4.57	5.58	17.28	19.68	21.92	24.73	26.76
12	3.07	3.57	4.40	5.23	6.30	18.55	21.03	23.34	26.22	28.30
13	3.57	4.11	5.01	5.89	7.04	19.81	22.36	24.74	27.69	29.82
14	4.07	4.66	5.63	6.57	7.79	21.06	23.68	26.12	29.14	31.32
15	4.60	5.23	6.26	7.26	8.55	22.31	25.00	27.49	30.58	32.80
16	5.14	5.81	6.91	7.96	9.31	23.54	26.30	28.85	32.00	34.27
17	5.70	6.41	7.56	8.67	10.08	24.77	27.59	30.19	33.41	35.72
18	6.26	7.01	8.23	9.39	10.86	25.99	28.87	31.53	34.81	37.16
19	6.84	7.63	8.91	10.12	11.65	27.20	30.14	32.85	36.19	38.58
20	7.43	8.26	9.59	10.85	12.44	28.41	31.41	34.17	37.57	40.00
21	8.03	8.90	10.28	11.59	13.24	29.62	32.67	35.48	38.93	41.40
22	8.64	9.54	10.98	12.34	14.04	30.81	33.92	36.78	40.29	42.80
23	9.26	10.20	11.69	13.09	14.85	32.01	35.17	38.08	41.64	44.18
24	9.89	10.86	12.40	13.85	15.66	33.20	36.42	39.36	42.98	45.56
25	10.52	11.52	13.12	14.61	16.47	34.38	37.65	40.65	44.31	46.93
26	11.16	12.20	13.84	15.38	17.29	35.56	38.88	41.92	45.64	48.29
27	11.81	12.88	14.57	16.15	18.11	36.74	40.11	43.19	46.96	49.64
28	12.46	13.56	15.31	16.93	18.94	37.92	41.34	44.46	48.28	50.99
29	13.12	14.26	16.05	17.71	19.77	39.09	42.56	45.72	49.59	52.34
30	13.79	14.95	16.79	18.49	20.60	40.26	43.77	46.98	50.89	53.67
40	20.71	22.16	24.43	26.51	29.05	51.81	55.76	59.34	63.69	66.77
60	35.53	37.48	40.48	43.19	46.46	74.40	79.08	83.30	88.38	91.95
120	83.85	86.92	91.58	95.70	100.62	140.23	146.57	152.21	158.95	163.65

For $n > 120$, $\chi^2_{n,\alpha} \approx n\left[1 - \frac{2}{9n} + z_\alpha\sqrt{\frac{2}{9n}}\right]^3$ where z_α is the desired percentage point for a standardized normal distribution.

4.1.2.5 Student t Distribution - This is a probability distribution of a random variable:

$$t_n = \frac{Z}{\sqrt{y/n}}$$

Z = random variable with normal distribution; with zero mean and unit variance

y = a variable with a Chi Square Distribution

n = number of degrees of freedom of the variable t_n. Values of this distribution are tabulated in Table 4.3.

4.1.2.6 Determination of the Type of Distribution - To apply statistics, the type of distribution must be determined. There are both graphical and numerical techniques to accomplish this (3).

1. Graphical Procedure for Small Number of Samples (N<30).

Step 1. Arrange the data in increasing order of magnitude (smallest first, largest last) and assign a ranking number (m) to each value based on its order of magnitude (Table 4.4 column 3).

Step 2. Calculate the percent probability for each value using one of the following two equations:

$$p = \left(\frac{m}{n+1}\right) 100$$

$$p = \left(\frac{2m-1}{2n}\right) 100$$

where

p = probability (percent) of being less than or equal to the chosen value

m = assigned number based on order of magnitude

n = total number of samples

Step 3. Plot each value versus its corresponding percent probability on probability paper (or log probability paper if data is log normally distributed).

Table 4.3. PERCENTAGE POINTS OF STUDENT t DISTRIBUTION (2)

Value of $t_{n;\alpha}$ such that $\text{Prob}[t_n > t_{n;\alpha}] = \alpha$

	α				
n	0.10	0.050	0.025	0.010	0.005
1	3.078	6.314	12.706	31.821	63.657
2	1.886	2.920	4.303	6.965	9.925
3	1.638	2.353	3.182	4.541	5.841
4	1.533	2.132	2.776	3.747	4.604
5	1.476	2.015	2.571	3.365	4.032
6	1.440	1.943	2.447	3.143	3.707
7	1.415	1.895	2.365	2.998	3.499
8	1.397	1.860	2.306	2.896	3.355
9	1.383	1.833	2.262	2.821	3.250
10	1.372	1.812	2.228	2.764	3.169
11	1.363	1.796	2.201	2.718	3.106
12	1.356	1.782	2.179	2.681	3.055
13	1.350	1.771	2.160	2.650	3.012
14	1.345	1.761	2.145	2.624	2.977
15	1.341	1.753	2.131	2.602	2.947
16	1.337	1.746	2.120	2.583	2.921
17	1.333	1.740	2.110	2.567	2.898
18	1.330	1.734	2.101	2.552	2.878
19	1.328	1.729	2.093	2.539	2.861
20	1.325	1.725	2.086	2.528	2.845
21	1.323	1.721	2.080	2.518	2.831
22	1.321	1.717	2.074	2.508	2.819
23	1.319	1.714	2.069	2.500	2.807
24	1.318	1.711	2.064	2.492	2.797
25	1.316	1.708	2.060	2.485	2.787
26	1.315	1.706	2.056	2.479	2.779
27	1.314	1.703	2.052	2.473	2.771
28	1.313	1.701	2.048	2.467	2.763
29	1.311	1.699	2.045	2.462	2.756
30	1.310	1.697	2.042	2.457	2.750
40	1.303	1.684	2.021	2.423	2.704
60	1.296	1.671	2.000	2.390	2.660
120	1.289	1.658	1.980	2.358	2.617

$\alpha = 0.995$, 0.990, 0.975, 0.950, and 0.900 follow from $t_{n;1-\alpha} = -t_{n;\alpha}$

An example of a data treatment is shown on Table 4.4 and Figure 4.4. If the data had a perfectly normal distribution, a straight line approximation would be obtained. In this case, the difference between the values at 84.13 and 15.87 percent probability would equal twice the standard deviation. If the data on both ends of the probability distribution tend to have a skew, a skewed distribution is more appropriate.

Example - A wastewater stream was surveyed for ten weeks of a year and the maximum daily concentrations of each week were recorded as shown in Table 4.4. The weeks of the survey were chosen randomly. Estimate the maximum daily concentration which would have a chance of being exceeded only once per year.

Since the sample size from which the maximum daily concentrations were taken is one week, the probability of a concentration being exceeded once during a year becomes

$$\alpha = 1/52 \text{ weeks} = 0.019 \approx 2 \text{ percent}$$

Then the probability of the concentration being less than or equal to the maximum is

$$p\,[X < X_s] = 1-\alpha = 98 \text{ percent}$$

The computational procedure is shown in Table 4.4 and the probabilistic plot is presented in Figure 4.4. From the graph the value X_s which has the percent probability of being exceeded only 1 week per year (2 percent) is 67.5 mg/l.

2. Graphical Procedure for Large Number of Samples (N>30).

For a large number of values it is convenient to rearrange the data in groups with the same range or intervals, e.g., 100-109 mg/l, 110-119 mg/l, 120-129 mg/l, etc., and to determine the number of values within each interval. The plot of the frequency of occurrence vs. the magnitude of the parameter is called a "histogram". The plot of the

Table 4.4. COMPUTATIONAL TABLE FOR GRAPHICAL NORMAL OR PEARSON TYPE III DISTRIBUTION DETERMINATION

Week of the year	X, Maximum daily concentration, mg/l	Increasing order of magnitude, m	Plotting position, $p=(\frac{m}{n+1})100$	X^2	X^3
3	52	8	72.73	2704	140603
7	33	2	18.18	1089	35937
12	41	5	45.45	1681	68921
18	59	10	90.91	3481	205379
22	37	3	27.27	1369	50653
29	32	1	9.09	1024	32768
31	47	7	63.66	2209	103823
36	38	4	36.36	1444	54872
37	57	9	81.82	3269	185193
49	45	6	54.55	2025	91125
	$\Sigma X_i = 441$	n=10		20275	969279

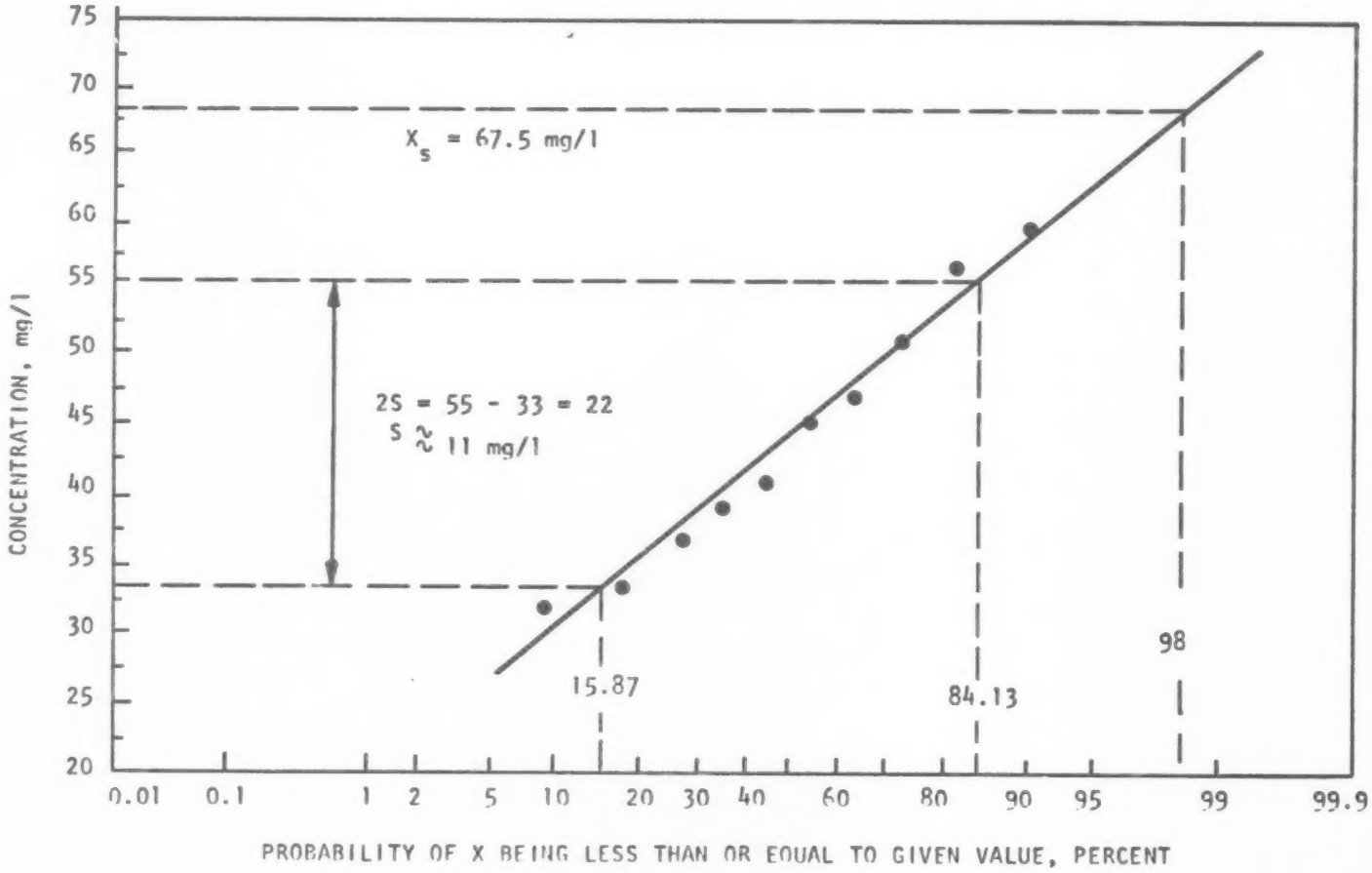


Figure 4.4. Graphical method for determining probability distribution

total number of cases being less than or equal to a given boundary value will yield the cumulative frequency distribution curve. Again, with the upper boundary approaching $+\infty$, the plotting position could be determined from the formula

$$p = \frac{m}{n + 1}$$

where m = number of cases with the same magnitude or lower.

Example - A wastewater stream was sampled each week for a period of one year and maximum daily concentrations were recorded as follows:

Concentration, mg/l	Frequency of Occurrence, f_i	$m = \Sigma f_i$	$p = \frac{m}{n+1} \times 100$
28-28.9	1	1	1.89
30-30.9	2	3	5.66
31-31.9	7	10	18.87
32-22.9	10	20	37.74
33-33.9	14	34	64.15
34-34.9	8	42	79.25
35-35.9	5	47	88.68
36-36.9	3	50	94.23
37-37.9	1	51	96.23
39-30.9	1	52	98.11
Totals	n = 52		

The plot of the histogram and the probability distribution function is presented in Figure 4.5.

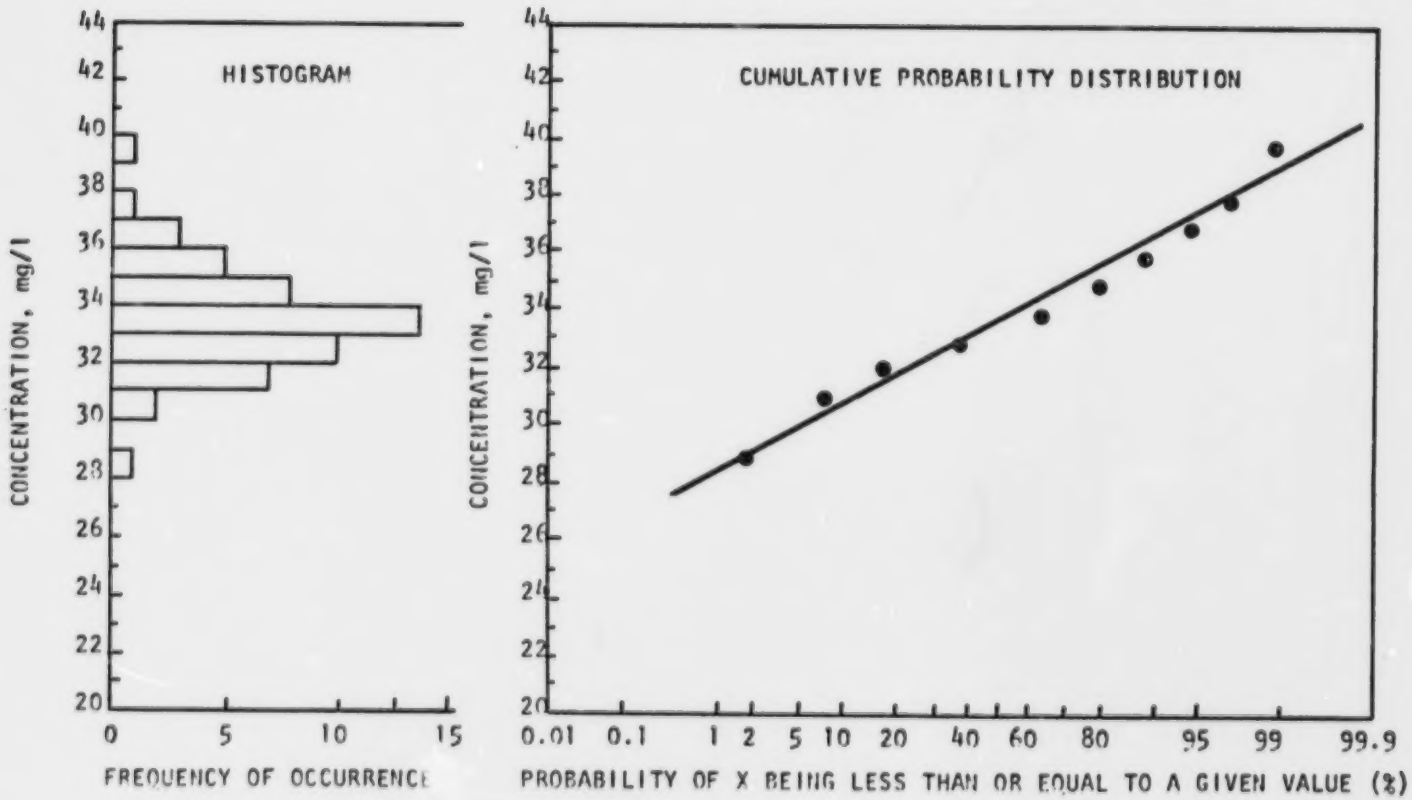


Figure 4.5. Histogram and probability distribution curve for larger number of samples

The Pearson Type III distribution requires the use of natural data or the logarithmic values of the natural data to compute the mean, standard deviation, and skew coefficient of the distribution. If logarithmic data is used, the method is called the log - Pearson Type III method (4).

The skew coefficient reveals the degree to which the distribution is asymetrical. A skew coefficient of zero indicates a symmetrical distribution of values. A normal distribution has a zero coefficient of skewness. A positive coefficient indicates that values above the mean tend to lie further from the mean than those below the mean.

Sparr and Hann (5) recommended the following relation between the coefficient of skewness and type of the best probability distribution.

Skew Coefficient, $\lvert g \rvert$	Best Fitting Probability Distribution
<0.5	normal
0.9-1.6	Pearson Type III
>1.7	log - normal

The method for obtaining the probability distribution using the Pearson Type III curve involves calculation of the skew coefficient and can be illustrated using the data given in Table 4.4.

1. Compute the mean

$$\bar{X} = \frac{\Sigma X}{N} = \frac{441}{10} = 44.1$$

2. Compute the standard deviation

$$S = \sqrt{\frac{\Sigma X^2 - (\Sigma X)^2/N}{N - 1}} = \sqrt{\frac{20275 - 441^2/10}{10 - 1}} = 9.59$$

3. Compute the coefficient of skewness

$$g = \frac{N^2\Sigma X^3 - 3N\Sigma X\Sigma X^2 + 2(\Sigma X)^3}{N(N-1)\ (N-2)\ S^3}$$

$$= \frac{(10^2 \times 9699279) - (3 \times 10 \times 441 \times 20275) + (2 \times 441^3)}{10(10-1)\ (10-2) \times 9.59^3}$$

$$= 0.35$$

For a skew coefficient of 0.35, the best fitting distribution is the normal.

The value X_s having a percent chance of being exceeded only once (weekly average) per year ($\alpha = 1/52 = 0.02$) can be calculated from the equation

$$X_s = \bar{X} + kS$$

with k taken from Table 4.5 for $g = 0.35$ and $\alpha = 2\%$. For $g = 0.35$, k must be extrapolated between 2.211 and 2.261:

$$k = \frac{2.261 + 2.211}{2} = 2.236$$

Then $$X_s = 44.0 + 2.236 \times 9.59 = 65.4 \text{ mg/l}$$

4.2 DETERMINATION OF NUMBER OF SAMPLES (6)

The number of samples necessary to reasonably characterize a water or wastewater is determined after collecting some background data on the concentration and variance of the parameters under consideration. These values can be estimated; however, estimation will decrease the confidence in the results. Two techniques can be used to calculate the number of samples, one based on the allowed sample variability, the other on the accuracy of the sample mean. Each will give a desired value of N with the largest value to be chosen for application.

4.2.1 Determining Sample Size from a Constraint on the Variability

To apply this method the following information is needed:

Table 4.5. K VALUES FOR POSITIVE SKEW COEFFICIENTS (7)

Skew Coefficient (g)	Percent Chance α										
	99	95	90	80	50	20	10	4	2	1	0.5
3.0	-0.667	-0.665	-0.660	-0.636	-0.396	0.420	1.180	2.278	3.152	4.051	4.970
2.9	-0.690	-0.688	-0.681	-0.651	-0.390	0.440	1.195	2.277	3.134	4.013	4.909
2.8	-0.714	-0.711	-0.702	-0.666	-0.384	0.460	1.210	2.275	3.114	3.973	4.847
2.7	-0.740	-0.736	-0.724	-0.681	-0.376	0.479	1.224	2.272	3.093	3.932	4.783
2.6	-0.769	-0.762	-0.747	-0.696	-0.368	0.499	1.238	2.267	3.071	3.889	4.718
2.5	-0.799	-0.790	-0.771	-0.711	-0.360	0.518	1.250	2.262	3.048	3.845	4.652
2.4	-0.832	-0.819	-0.795	-0.725	-0.351	0.537	1.262	2.256	3.023	3.800	4.584
2.3	-0.867	-0.850	-0.819	-0.739	-0.341	0.555	1.274	2.248	2.997	3.753	4.515
2.2	-0.905	-0.882	-0.844	-0.752	-0.330	0.574	1.284	2.240	2.970	3.705	4.444
2.1	-0.946	-0.914	-0.869	-0.765	-0.319	0.592	1.294	2.230	2.942	3.656	4.372
2.0	-0.990	-0.949	-0.895	-0.777	-0.307	0.609	1.302	2.219	2.912	3.605	4.298
1.9	-1.037	-0.984	-0.920	-0.788	-0.294	0.627	1.310	2.207	2.881	3.553	4.223
1.8	-1.087	-1.020	-0.945	-0.799	-0.282	0.643	1.318	2.193	2.848	3.499	4.147
1.7	-1.140	-1.056	-0.970	-0.808	-0.268	0.660	1.324	2.179	2.815	3.444	4.069
1.6	-1.197	-1.093	-0.994	-0.817	-0.254	0.675	1.329	2.163	2.780	3.388	3.990
1.5	-1.256	-1.131	-1.018	-0.825	-0.240	0.690	1.333	2.146	2.743	3.330	3.910
1.4	-1.318	-1.168	-1.041	-0.832	-0.225	0.705	1.337	2.128	2.706	3.271	3.828
1.3	-1.383	-1.206	-1.064	-0.838	-0.210	0.719	1.339	2.108	2.666	3.211	3.745
1.2	-1.449	-1.243	-1.086	-0.844	-0.195	0.732	1.340	2.087	2.626	3.149	3.661
1.1	-1.518	-1.280	-1.107	-0.848	-0.180	0.745	1.341	2.066	2.585	3.087	3.575
1.0	-1.588	-1.317	-1.128	-0.852	-0.164	0.758	1.340	2.043	2.542	3.022	3.489
.9	-1.660	-1.353	-1.147	-0.854	-0.148	0.769	1.339	2.018	2.498	2.957	3.401
.8	-1.733	-1.388	-1.166	-0.856	-0.132	0.780	1.336	1.993	2.453	2.891	3.312
.7	-1.806	-1.423	-1.183	-0.857	-0.116	0.790	1.333	1.967	2.407	2.824	3.223
.6	-1.880	-1.458	-1.200	-0.857	-0.099	0.800	1.328	1.939	2.359	2.755	3.132
.5	-1.955	-1.491	-1.216	-0.856	-0.083	0.808	1.323	1.910	2.311	2.686	3.041
.4	-2.029	-1.524	-1.231	-0.855	-0.066	0.816	1.317	1.880	2.261	2.615	2.949
.3	-2.104	-1.555	-1.245	-0.853	-0.050	0.824	1.309	1.849	2.211	2.544	2.856
.2	-2.178	-1.586	-1.258	-0.850	-0.033	0.830	1.301	1.818	2.159	2.472	2.763
.1	-2.252	-1.616	-1.270	-0.846	-0.017	0.836	1.292	1.785	2.107	2.400	2.670
0	-2.326	-1.645	-1.282	-0.842	0	0.842	1.282	1.751	2.054	2.326	2.576

Table 4.6. K VALUES FOR NEGATIVE SKEW COEFFICIENTS (7)

Skew Coefficient (g)	Percent Chance										
	99	95	90	80	50	20	10	4	2	1	0.5
0	-2.326	-1.645	-1.282	-0.842	0	0.842	1.282	1.751	2.054	2.326	2.576
- .1	-2.400	-1.673	-1.292	-0.836	0.017	0.846	1.270	1.716	2.000	2.252	2.482
- .2	-2.472	-1.700	-1.301	-0.830	0.033	0.850	1.258	1.680	1.945	2.178	2.338
- .3	-2.544	-1.726	-1.309	-0.824	0.050	0.853	1.245	1.643	1.890	2.104	2.294
- .4	-2.615	-1.750	-1.317	-0.816	0.066	0.855	1.231	1.606	1.834	2.029	2.201
- .5	-2.686	-1.774	-1.323	-0.808	0.083	0.856	1.216	1.567	1.777	1.955	2.108
- .6	-2.755	-1.797	-1.328	-0.800	0.099	0.857	1.200	1.528	1.720	1.880	2.016
- .7	-2.824	-1.819	-1.333	-0.790	0.116	0.857	1.183	1.488	1.663	1.806	1.926
- .8	-2.891	-1.839	-1.336	-0.780	0.132	0.856	1.166	1.448	1.606	1.733	1.837
- .9	-2.957	-1.858	-1.339	-0.769	0.148	0.854	1.147	1.407	1.549	1.660	1.749
-1.0	-3.022	-1.877	-1.340	-0.758	0.164	0.852	1.128	1.366	1.492	1.588	1.664
-1.1	-3.087	-1.894	-1.341	-0.745	0.180	0.848	1.107	1.324	1.435	1.518	1.581
-1.2	-3.149	-1.910	-1.340	-0.732	0.195	0.844	1.086	1.282	1.379	1.449	1.501
-1.3	-3.211	-1.925	-1.339	-0.719	0.210	0.838	1.064	1.240	1.324	1.383	1.424
-1.4	-3.271	-1.938	-1.337	-0.705	0.225	0.832	1.041	1.198	1.270	1.318	1.351
-1.5	-3.330	-1.951	-1.333	-0.690	0.240	0.825	1.018	1.157	1.217	1.256	1.282
-1.6	-3.388	-1.962	-1.329	-0.675	0.254	0.817	0.994	1.116	1.166	1.197	1.216
-1.7	-3.444	-1.972	-1.324	-0.660	0.268	0.808	0.970	1.075	1.116	1.140	1.155
-1.8	-3.499	-1.981	-1.318	-0.643	0.282	0.799	0.945	1.035	1.069	1.087	1.097
-1.9	-3.553	-1.989	-1.310	-0.627	0.294	0.788	0.920	0.996	1.023	1.037	1.044
-2.0	-3.605	-1.996	-1.302	-0.609	0.307	0.777	0.895	0.959	0.980	0.990	0.995
-2.1	-3.656	-2.001	-1.294	-0.592	0.319	0.765	0.869	0.923	0.939	0.946	0.949
-2.2	-3.705	-2.006	-1.284	-0.574	0.330	0.752	0.844	0.888	0.900	0.905	0.907
-2.3	-3.753	-2.009	-1.274	-0.555	0.341	0.739	0.819	0.855	0.864	0.867	0.869
-2.4	-3.800	-2.011	-1.262	-0.537	0.351	0.725	0.795	0.823	0.830	0.832	0.833
-2.5	-3.845	-2.012	-1.250	-0.518	0.360	0.711	0.771	0.793	0.798	0.799	0.800
-2.6	-3.889	-2.013	-1.238	-0.499	0.368	0.696	0.747	0.764	0.768	0.769	0.769
-2.7	-3.932	-2.012	-1.224	-0.479	0.376	0.681	0.724	0.738	0.740	0.740	0.741
-2.8	-3.973	-2.010	-1.210	-0.460	0.384	0.666	0.702	0.712	0.714	0.714	0.714
-2.9	-4.013	-2.007	-1.195	-0.440	0.390	0.651	0.681	0.683	0.689	0.690	0.690
-3.0	-4.051	-2.003	-1.180	-0.420	0.396	0.636	0.660	0.666	0.666	0.667	0.667

1. Allowable error of the standard deviation (or the difference from its true value) - $\frac{\Omega}{S}$

2. Confidence level required - $(1-\alpha)$

Therefore, for this situation, one is estimating that the value of a certain variable will occur within a specific interval. A normal distribution of the data around the mean is assumed. The data should be checked for normality by plotting on probability graph paper.

Example - Determine the number of samples required from a wastewater monitoring program such that the estimated standard deviation will be within 25% of its true value ($\pm$ 12.5% of estimated value) at a confidence level of 98%.

$$\alpha = 1 - 0.98 = 0.02 \qquad \frac{\Omega}{S} = 0.25$$

From Figure 4.6, the value of $\frac{\Omega}{S} = 0.25$ is found on the Y (vertical) axis and a horizontal line is followed until the 98% confidence (corresponds to $\alpha = 0.02$) curve is met. Then a vertical line is dropped to the X (horizontal) azis to find the number of samples. In this case N = 180 samples.

4.2.2. Determining Sample Size from a Constraint on the Mean Value

To apply this method, the following information is required:

1. Confidence level required - $(1 - \alpha)$

2. Coefficient of variation of the source to be sampled - CV

3. Allowable accuracy of the average from the true mean of the source.

A double iteration procedure should be used especially if the number of samples is found to be small ($N < 30$).

The applicable equation is:

$$N = \left(\frac{CV \cdot Z_{\alpha/2}}{\beta/100}\right)^2$$

where: $CV = \frac{S_x}{\bar{X}}$ = coefficient of variation

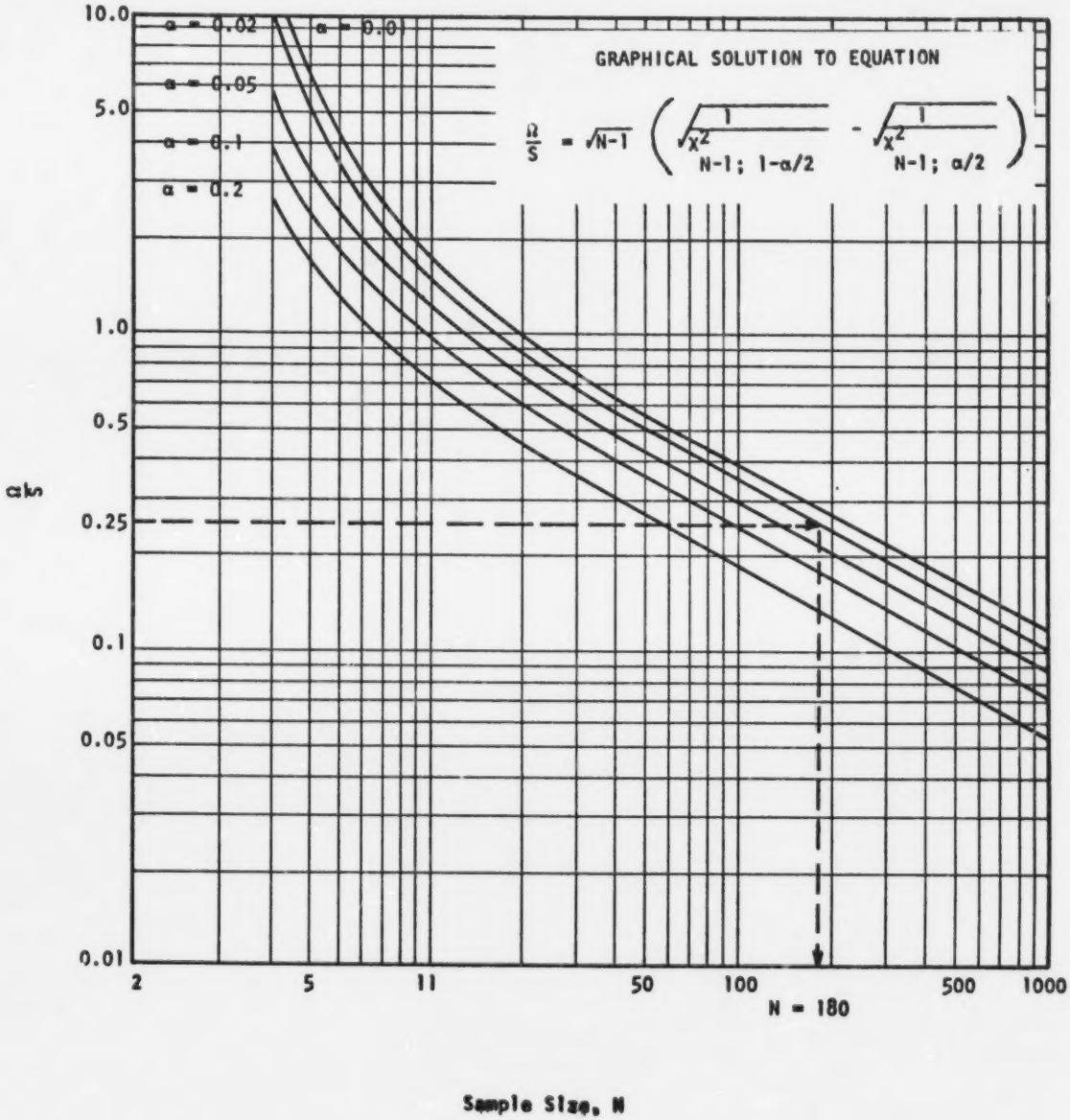


Figure 4.6. Determination of the number of samples based on the required accuracy of extreme values

S_x = standard deviation

$\bar{X}$ = mean

β = allowed deviation of the average value from the true mean in percent

$Z_{\alpha/2}$ = probablistic variable of normal distribution at a confidence level $1 - \alpha$.

Estimations of CV, S_x, $\bar{X}$ can be used. For this calculation a normal distribution is assumed.

Example - For a wastewater stream with an average daily concentration, $\bar{X}$ = 120 mg/l BOD, with a standard deviation, S_x = 32 mg/l, determine the number of daily samples which would provide accuracy of the daily averages within 5%.

$\beta = 5\%$

$$CV = \frac{S_x}{\bar{X}} = \frac{32}{120} = 0.27$$

At 95% confidence interval $Z_{\alpha/2}$ = 1.96 (From Table 4.1).

Step 1. $$N = \left(\frac{CV \cdot Z_{\alpha/2}}{\beta/100}\right)^2 = \left(\frac{0.27 \cdot 1.96}{0.05}\right)^2 = 109.27$$

= 110 samples

Step 2. Using N = 110, find $t_{\alpha/2,N-1}$ from Table 4.3:

$$t_{(0.025,109)} = 1.983$$

$$N = \left(\frac{CV \cdot t_{.975}}{\beta/100}\right)^2 = \left(\frac{0.27 \cdot 1.983}{.05}\right)^2 = 114.6$$

= 115 samples

This problem can also be solved graphically. In Figure 4.7 the number of samples, N has been related to the parameter, $\beta/(100 \times CV)$.

$$\frac{\beta}{100 \times CV} = \frac{5}{100 \times 0.27} = 0.185$$

This value, 0.185, is found on the Y- axis and a horizontal line is followed until the 95% confidence (corresponds to $\alpha = 0.05$) curve is met. Then a vertical line is dropped to the X axis to find the number of samples. In this case N = 115 samples.

If both the accuracy of the standard deviation and the accuracy of the mean are used as criteria, choose the larger number of samples from the two calculations.

For the example, $N_s = 180$ and $N_{\bar{X}} = 115$; therefore, N = 180 samples would be chosen.

4.3 DETERMINATION OF SAMPLING FREQUENCY

The various techniques for determining sampling frequency have been evaluated and the method of spectral analysis has been chosen as the most applicable. Although it requires the use of a computer, spectral analysis should be applied whenever possible because of accuracy and simplicity in final interpretation (8, 9, 10).

4.3.1 Definition

Spectral analysis - The power spectra describes the general frequency composition of data in terms of the spectral density of its mean square value and is a plot of this spectral density function versus frequency. With this procedure, the distribution of the variance with frequency can be seen. Power spectra for 4 variations of X(t) are shown in Figure 4.8.

The relatively uniform and broad spectrum as is seen on Figure 4.8a is typical for randomly fluctuating records. If the signal is composed of two harmonics with the frequency $f_1 = \frac{1}{T_1}$, and $f_2 = \frac{1}{T_2}$ as illustrated in Figure 4.8-d, the peaks will appear at frequencies f_1 and f_2. As can be seen the resultant power spectrum is basically the summation of the power spectrum for a sine wave and random noise. Although the power spectral density of a sine wave is infinitely large at the frequency of the sine wave and zero at all other frequencies (see Figure 4.8-a), the integral of the power spectrum over any frequency range that includes the numerical frequency has a finite value equal to the mean square value of the sine wave, where X_m is the amplitude of the sine wave.

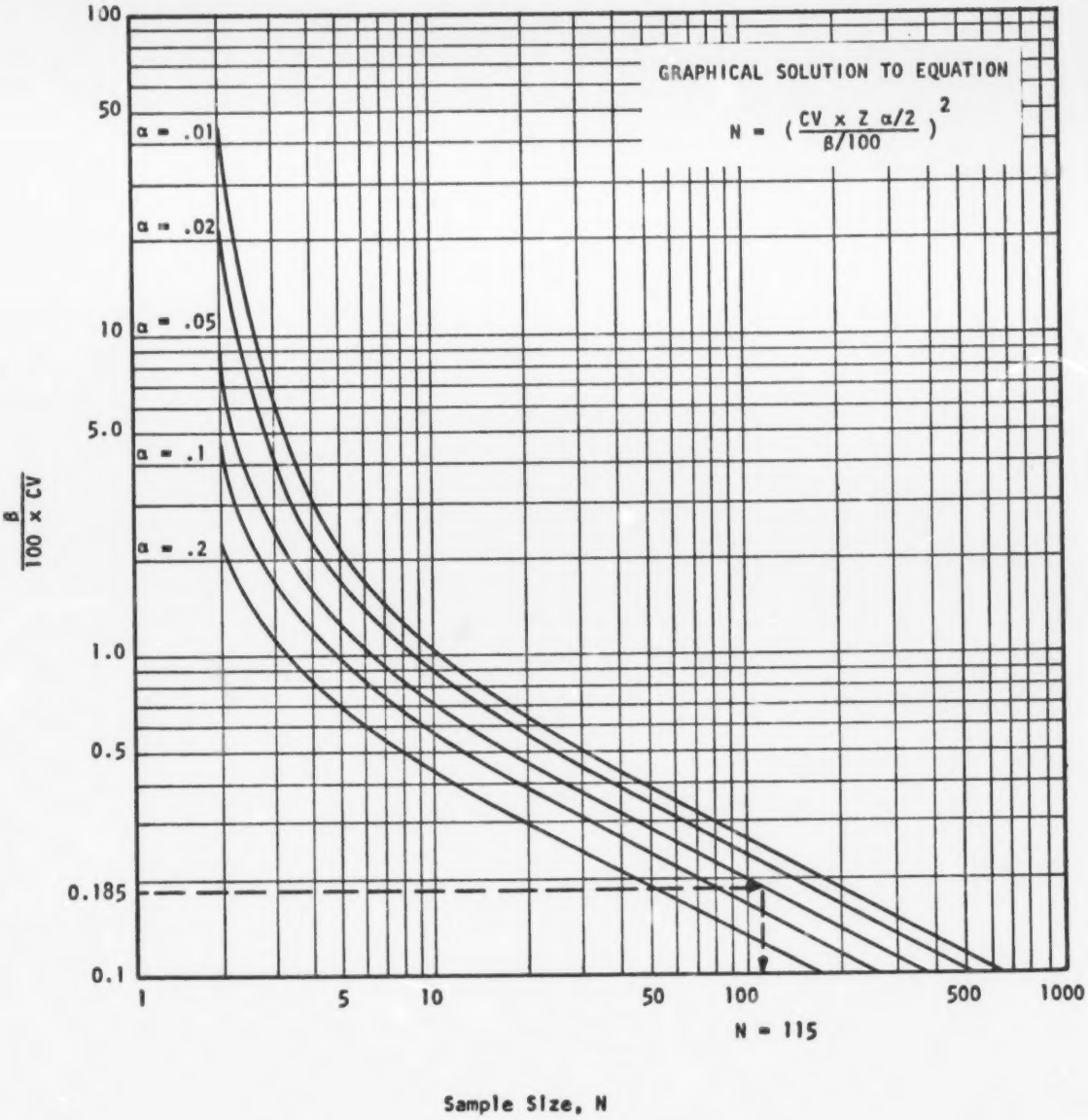


Figure 4.7. Determination of the number of samples based on the required accuracy of the mean

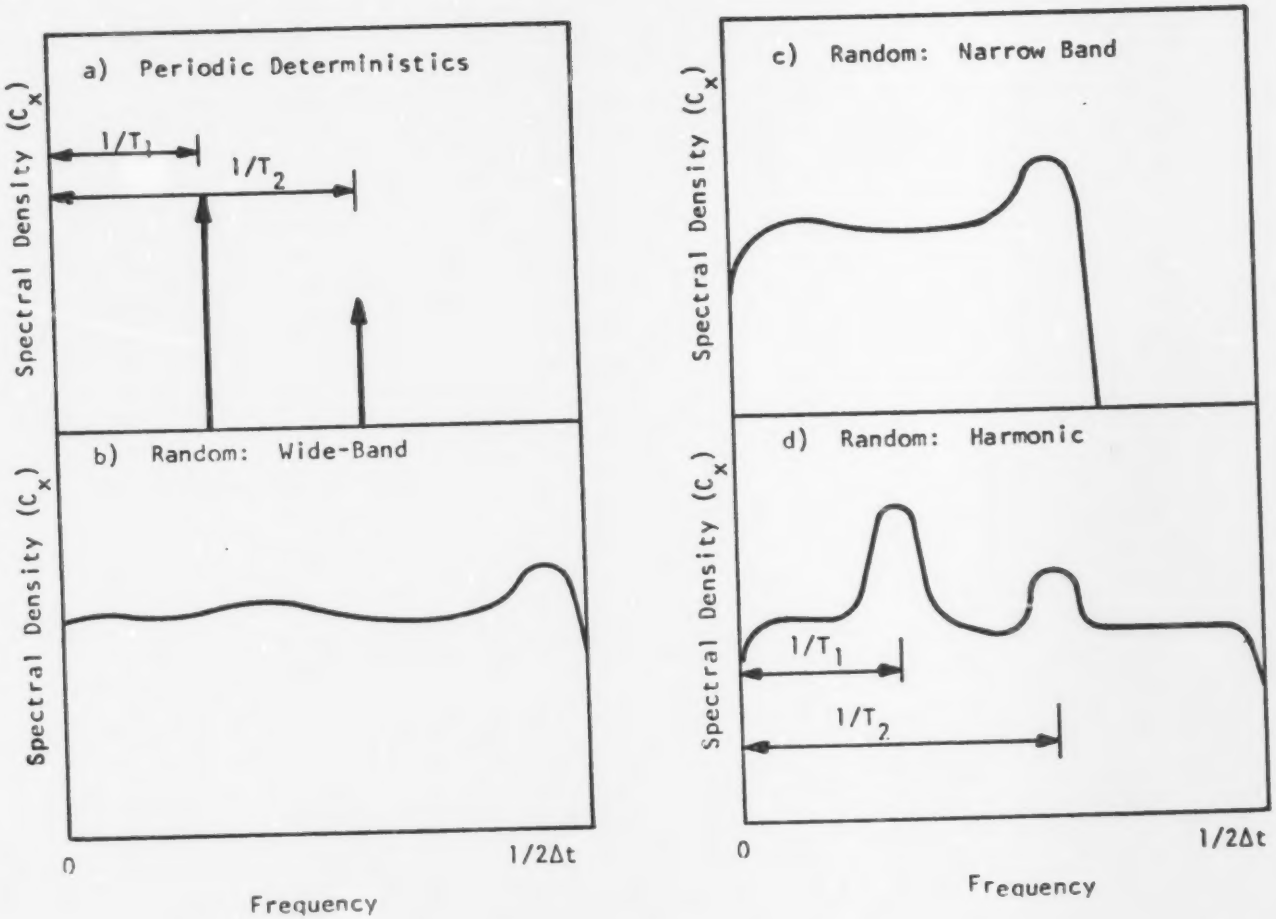


Figure 4.8. Various power spectra for variable X(t)

Since the variance of a sine wave equals $S^2 = X_m^2/2$ and the delta function representing the variance of the sine wave is located at the frequency of the sine wave, f_1, then $S^2 = \int (f_1)\, df$ or $S^2 = \int_f^{f+df} \Gamma\, df$.

This means that the area under the power spectrum curve corresponds to the variance of the signal. If another sine wave with frequency f + df was superimposed on the basic frequency, the total variance of the signal would be $S^2 = \int (f_1)\, df + \int (f_2)\, df$. If the signal was composited from a large number of sine waves then the total variance would become

$$S^2 = \int_0^{f_c} \Gamma df$$

where f_c is the maximal frequency detected on the signal.

Finally, the power spectra for "narrow band" random variation is terminated at a frequency $f_o = \frac{1}{2T} < f\ max = \frac{1}{2\Delta T}$. As seen in Figure 4.8-c, the power spectrum at the end is peaked similarly to that of a sine wave but it is continuous for frequencies $f_2 < f_o$. Again the area under the curve should equal the variance S_x^2 if the record has zero mean, otherwise it should equal $S_x^2 + \mu_x^2$.

It should be noted that for any discrete sampling the maximum frequency which can be resolved from the record is the Nyquist frequency; $f\ max = 1/(2\ \Delta t)$ where Δt is the sampling interval, and even the apparent effect of this frequency will be confounded by the accumulated effects for all larger frequencies.

4.3.2 Determination of the Sampling Frequency From Power Spectra

It is imperative that a good set of historical data be available for analysis. This data should be taken at a frequency that is higher than the expected harmonic variation component of the signal. For example, if daily trends are to be analyzed, hourly samples may be taken. Then the significance of any harmonic variability can be seen. In analyzing the power spectra to determine sampling frequency, the sampling frequency should be chosen just after the last significant peak on the power spectra as shown in Figure 4.9.

In general, two "practical rules of thumb" are important when analyzing times series data [11]:

1. The data should cover a time period 10 times the longest period of interest, e.g., 10 years of data if the annual period is of interest.
2. The sampling interval (time between data points) should be less than half the shortest period of interest. From hourly data, the shortest period that can be evaluated.

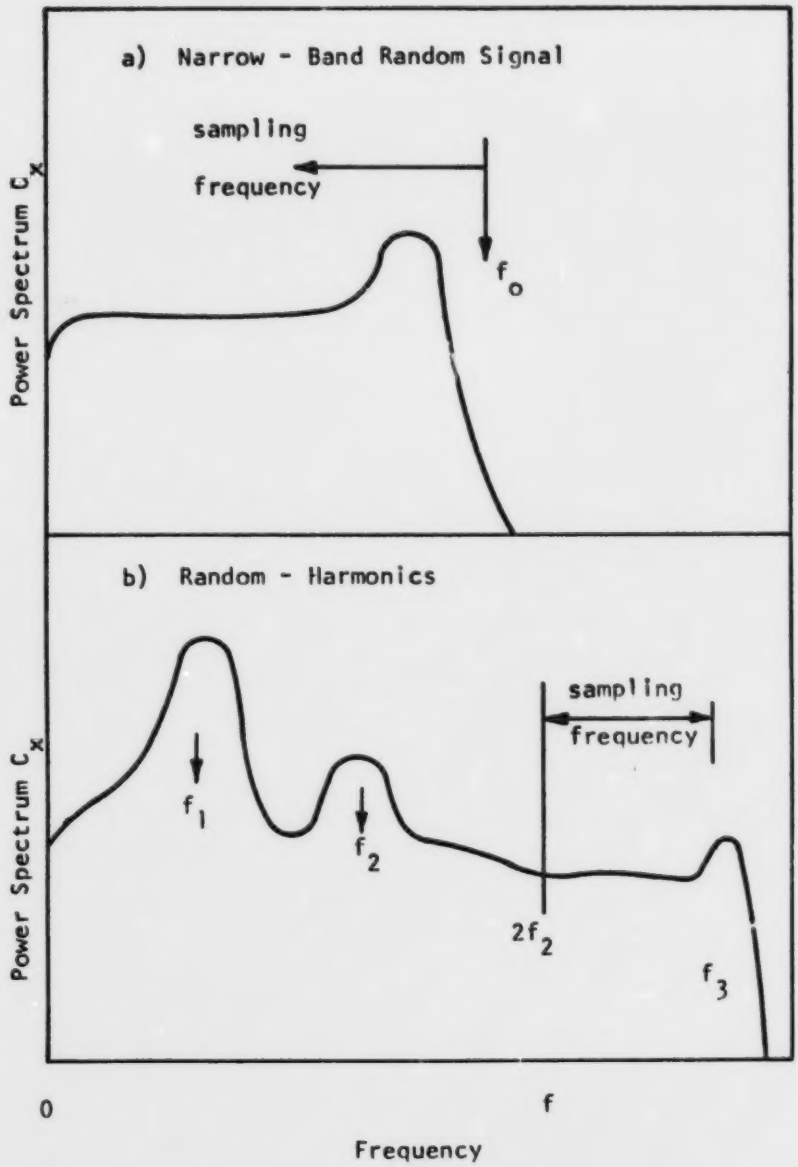


Figure 4.9. Determination of sampling frequency

is the effect of a two hour period. However, even the effect of this period is not clear because it includes the effect of shorter periods. The shortest period with a clearly defined effect would be the three hour period.

For the narrow-band random signal, the frequency can be theoretically anywhere below f_0. If harmonic components are present the frequency of sampling should be higher than the highest significant harmonic frequency multiplied by two. On Figure 4.9-b the sampling interval for a random-harmonic signal would be

$$\Delta t \leq \frac{1}{2f_x}$$

and the sampling frequency, f_s, should be within the interval

$$2f_2 < f_x = \frac{1}{\Delta t} \leq f_3$$

The following examples should clarify and further explain the power spectra applications.

Example 1 - The wastewater influent for the city of Racine, Wisconsin was sampled hourly in the summer of 1974 and the TOC analyzed. The record is shown in Figure 4.10. The average calculated was 70.56 mg/l and the variance was 1262.07 mg^2/l^2. Determine the optimum sample frequency for this plant.

Spectral analysis is performed on the data and the spectrum is plotted as shown in Figure 4.11. A computer program to obtain these results is included at the end of the chapter. It can be seen that the power spectrum confirms the 24 hour variability as shown in the correlogram. The finding indicates that most of the variability occurs within the frequency band 1/48 $hr.^{-1}$ to 1/16 $hr.^{-1}$ with a strong peak at the frequency 1/24 $hr.^{-1}$. Almost 85 percent of the variance, S_x^2, is caused by these low frequency fluctuations. There is also a less significant peak at the frequency 1/8 $hr.^{-1}$. The rest of the record shows the effect of random fluctuations.

The sampling frequency should be two times the frequency just after the last significant variation or peak.

In this situation the last significant variation is at 1/16 $hr.^{-1}$ (or 1 sample every 16 hours). Since this is the Nyquist frequency, the sampling frequency should be twice as often or 2 x 1/16 $hr.^{-1}$ = 1/8 $hr.^{-1}$ (one sample every 8 hours). This would reveal almost 100% of the wastewater variability over a sufficient length of time.

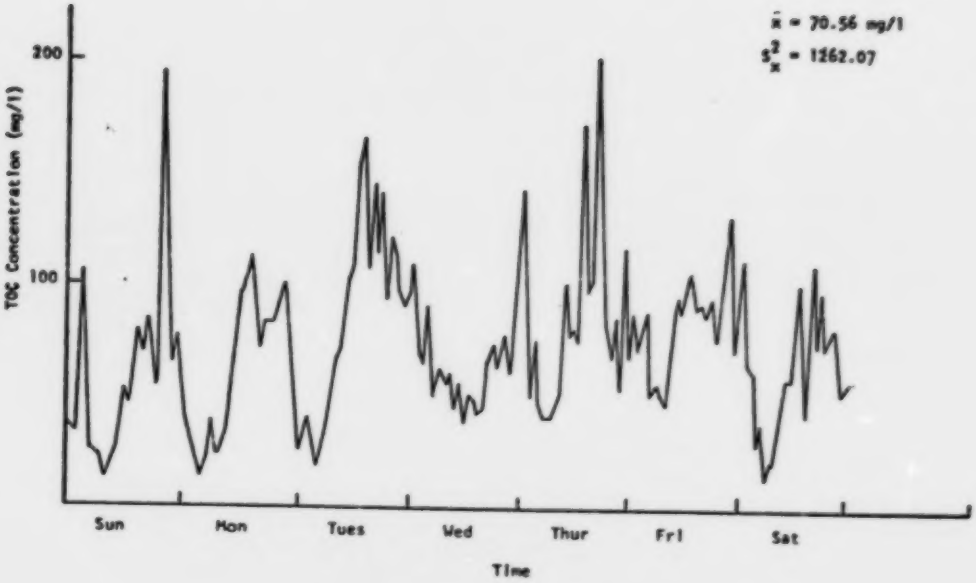


Figure 4.10. Time record of TOC of municipal wastewater at Racine, Wisconsin

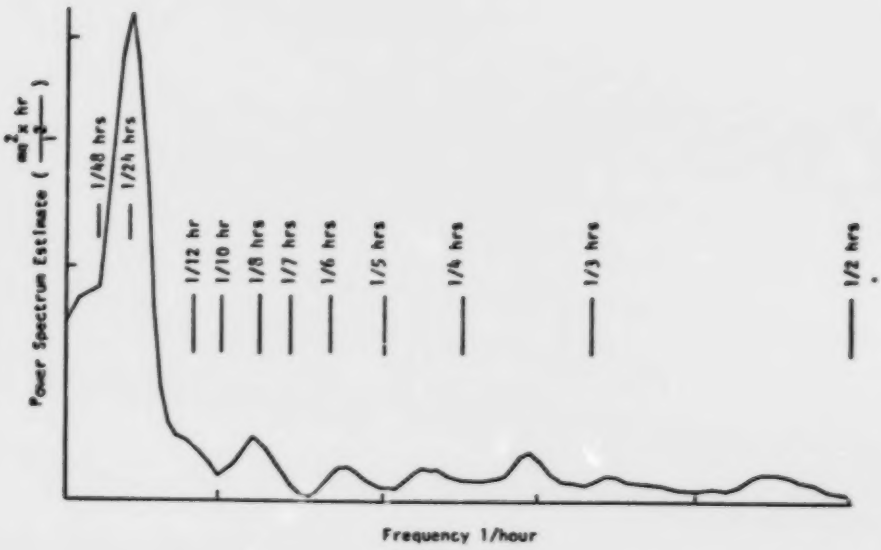


Figure 4.11. Power spectrum of TOC concentration of municipal wastewater at Racine, Wisconsin

Example 2 - The spectra of wastewater variations typical for two types of industrial discharges are presented in Figures 4.12 and 4.13. Determine the optimum frequency for sampling.

On figure 4.12, a strong period occurs in the frequency band 1/16 hr^{-1} to 1/8 hr^{-1} with a secondary peak in the frequency band 1/6 hr^{-1} to 1/5 hr^{-1}. This spectrum is typical for industrial plants working 24 hours, 7 days a week with three shifts a day. Note that almost no low frequency or trend has been detected. Thus, the data seems to be stationary. Therefore, the most feasible sampling program would be twice the frequency just after the last significant peak. In this case the last peak occurred from 1/6 $hour^{-1}$ to 1/5 $hour^{-1}$ and the frequency just beyond is 1/4 hr^{-1}. Therefore, the sampling frequency would be 2 x 1/4 hr^{-1} or one sample every 2 hours.

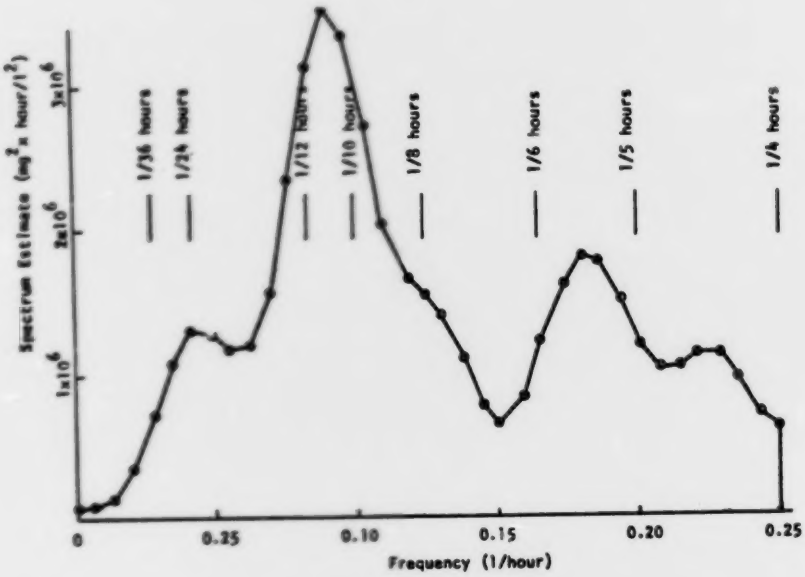


Figure 4.12 Power spectrum of chemical plant discharge, Case 1

Another chemical plant discharge, the spectrum of which is shown in Figure 4.13, shows a strong harmonic at the frequency 1/24 hr^{-1}, which is typical for plants working mainly with one daily shift. There are also a secondary peaks at frequencies 1/12 hr^{-1} and 1/6 hr^{-1}. Following the same theory, sampling could be scheduled at frequencies of 1 sample per 12 hours. However, since the peak at 1/6 hr^{-1} is somewhat large, a more accurate program would require samples once every 3 hours.

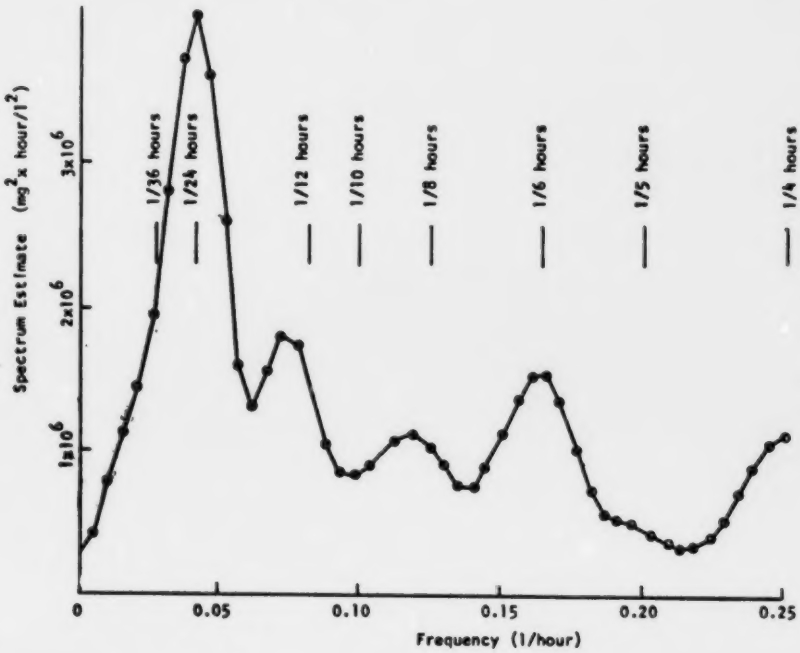


Figure 4.13 Power spectrum of chemical plant discharge, Case II

4.4 DETERMINATION OF PARAMETERS TO ANALYZE

The decision regarding which parameters to analyze is critical since it determines the value of sample, allowable holding time, preservation method, etc. There are two statistical methods to resolve this problem if prior regulations do not exist. The decision variable for the first method is the probability of exceeding a standard, and the second is the correlation between parameters.

4.4.1 Probability of Exceeding a Standard

This technique requires
1. Knowledge (or estimates) of the mean - $\bar{X}$
2. Knowledge (or estimates) of the standard deviation - S_x
3. Value not to be exceeded - X_s

The probability of exceeding the standard is:

$$p\ (X > X_s) = \text{prob}\ (Z > Z_\alpha) = \alpha$$

where

$$Z_\alpha = \frac{X_s - \bar{X}}{S_x}$$

For a computed Z_α, the probability can be found in Table 4.1. Parameters with the highest $p(X > X_s)$ have the highest priorities of sampling.

Example - The effluent standard for an industry was determined to be 100 mg/l of Cl^-. A wastewater quality survey has shown that the mean concentration of chlorides $\bar{X}$, was 75 mg/l and the standard deviation S_x, was 18 mg/l.

The probability of the standard being exceeded can be computed as follows:

Determine Z_α

$$Z_\alpha = \frac{X_s - \bar{X}}{S_x} = \frac{100 - 75}{18} = 1.39$$

From Table 4.1 for $Z_\alpha = 1.39$ the probability $p\ (X > X_s)$ is 0.823 or 8.23 percent.

Often an effluent standard will be specified for several parameters. Then the parameters can be ranked in descending order of their probability of being exceeded. The priority of sampling will be in the same order. An example of how this can be done in practice is given in Table 4.7.

Table 4.7. SAMPLING PRIORITIES OF PARAMETERS FOR A TYPICAL WASTEWATER

Parameter	Water Quality Standard, X_s	Mean, $\bar{X}$	Standard Deviation, S	Z	$p(x > x_s)$	Sampling Priority
pH	6.5 - 8.0	7.8	0.4	0.50	0.308	5
TOC	None	31	7.9	-	0	16-22
COD	70	60	11	0.91	0.181	7
BOD	30	20	8	1.25	0.125	9-10
TKN	5	3.5	1.5	1.00	0.158	8
Phosphates	1	0.5	0.2	2.50	0.006	15
Conductivity	None	320	80	-	0	16-22
Total dissolved solids	500	491	125	0.072	0.472	1
Suspended solids	30	28	5	0.40	0.34	4
Turbidity	20	19	3	0.33	0.37	3
Lead	5	3	1.0	2.0	0.0228	14
Mercury	5	2.5	1.5	1.67	0.047	13
Iron	10	7.8	1.9	1.16	0.123	11
Copper	7	0.8	0.15	1.33	0.0918	12
Alkalinity	None	-	-	-	0	16-22
Acidity	None	-	-	-	0	16-22
Calcium	None	-	-	-	0	16-22
Hardness	None	-	-	-	0	16-22
Magnesium	None	-	-	-	0	16-22
Total coliforms	100	81	65	0.29	0.386	2
Fecal coliforms	10	5	64	1.25	0.125	9-10
Chlorides	200	156	59	0.90	0.184	6

4.4.2 Correlation Between Measured Parameters (12)

Another method is to evaluate the closeness of correlation among the water quality parameters of interest. It is known that a correlation exists between many water quality parameters such as:

BOC_5 and TOC
COD and TOC
Chlorides and Conductivity
Total dissolved solids and conductivity
Suspended solids and turbidity
Acidity, alkalinity and pH
Hardness, calcium and magnesium
Hardness, and alkalinity

The statistical relationship is not limited to chemical water quality indicators but it can also be extended to some biological and bacteriological parameters. If a strong correlation exists between two or more parameters, the monitoring of one parameter may be discontinued or monitored at a reduced frequency. In order to apply the technique, the following must be available:

1. A data record for all parameters of interest.

2. A computer program for calculating correlation coefficients.

The relationship between two parameters x and y can be linear or non-linear (such as logarithmic, exponential, etc.) If a non-linear relationship seems to exist, attempt to linearize the relationship, e.g., by using logarithms of the values of x and y or some other functional approximation. Then linear regression analysis provides the linear functional relationship in the form:

$$\tilde{Y} = a + b\tilde{x}$$

Where a and b are the intercept and regression coefficient (slope), respectfully, of the line of best fit. The coefficient of correlation, ρ_{xy}, will then be a measure of the closeness of the fit.

Figure 4.14 shows and example of the relationship of BOD to TOC for the Racine, Wisconsin wastewater. In practice, the available data will be limited to a sample of N pairs of observed values for x and y.

Only estimates of a and b can be determined based on this limited data. The following equations can be used to obtain these estimates.

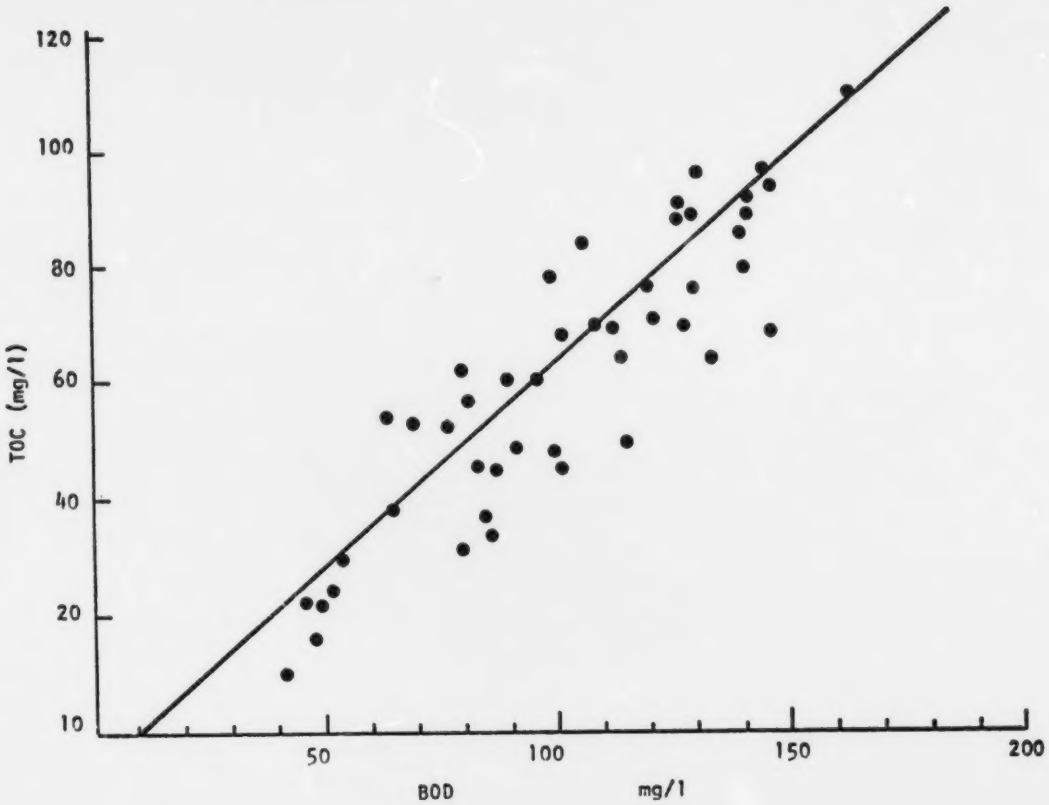


Figure 4.14. Relationship of TOC-BOD concentrations of a municipal wastewater

$$a = \bar{Y} - b\bar{X}$$

$$b = \frac{\sum_{i=1}^{N} (x_i - \bar{X})\, y_i}{\sum_{i=1}^{N} (x_i - \bar{X})^2} = \frac{\sum_{i=1}^{N} x_i\, y_i - N\bar{X}\bar{Y}}{\sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2 / N}$$

N = number of pairs of x_i and y_i

$\bar{Y}$ = mean of y_i's

$\bar{X}$ = mean of x_i's

The coefficient of correlation can be determined from the equation:

$$\rho_{xy} = \frac{\Sigma_{i=1}^{N} (x_i - \bar{X})\,(y_i - \bar{Y})}{[\Sigma_{i=1}^{N} (x_i - \bar{X})^2 \;\; \Sigma_{i=1}^{N} (y_i - \bar{Y})^2]^{1/2}}$$

$$\sigma = \frac{\Sigma_{i=1}^{N} x_i y_i - N\bar{X}\bar{Y}}{[(\Sigma_{i=1}^{N} x_i^{\,2} - N\bar{X}^2) \quad (\Sigma_{i=1}^{N} y_i^{\,2} - N\bar{Y}^2)]^{1/2}}$$

Numerous computer package subroutines are available for the above analysis.

The hypothesis that a relationship between x and y exists can be tested at a given level of significance α ($1 - \alpha$ = confidence that the hypothesis holds). If the obtained $|\rho_{xy}| > \rho_c$ where ρ_c is the minimal correlation coefficient from Table 4.8, the zero correlation hypothesis (i.e., that there is no relationship) is rejected. For a perfect fit $|\rho_{xy}| = 1$.

It is convenient to arrange the results in a matrix as is done in the example (Table 4.9).

The pairs with high coefficients of correlation signifcantly greater than the critical correlation coefficient are eligible for selective elimination of one of the parameters of the pair or for reduction of the frequency of the data acquisition. The decision on which parameter should be eliminated will be based on cost of the data acquisition and the priority of the parameter.

Example. A wastewater system was surveyed for an extended period of time. As a result of the survey, 25 sets of wastewater quality data was gathered. Each set contained data on pH, TOC, COD, BOD, TKN, phosphorus, conductivity, total dissolved solids, suspended solids, turbidity, lead, mercury, iron, copper, alkalinity, acidity, hardness, calcium, magnesium, coliform bacteria, fecal coliform, and chlorides.

1. Determine the sampling priority of each parameter
2. Determine which parameter measurements can be eliminated or reduced.

Determine the probability that the standard for each parameter exceeded $p(X > X_s) = \alpha$. This will determine the sampling priority of the parameter to be monitored. The priority is given by the descending order of the magnitude of $p(X > X_s)$.

The correlation analysis of the above 22 parameters was performed by a computer according to the previous equations. The analysis provided the following information:

Intercept, a_{xy}

Regression coefficient, b_{xy}

Correlation coefficient, ρ_{xy}

Theoretically, for all 22 parameters, $1/2(22^2 - 22)$ computations would be required, but professional judgment will eliminate the obviously uncorrelated pairs.

The critical correlation coefficient for N = 25 can be obtained from Table 4.8.

Table 4.8. VALUES OF CORRELATION COEFFICIENT, ρ, FOR TWO LEVELS OF SIGNIFICANCE (13)

Degrees of Freedom	Percent Level of Significance, α	
n=N-1	Five	One
1	0.997	1.000
2	0.950	0.990
3	0.878	0.959
4	0.811	0.917
5	0.754	0.874
6	0.707	0.834
7	0.666	0.798
8	0.632	0.765
9	0.602	0.735
10	0.576	0.708
11	0.553	0.684
12	0.532	0.661
13	0.514	0.641
14	0.497	0.623
15	0.482	0.606
16	0.468	0.590
17	0.456	0.575
18	0.444	0.561
19	0.433	0.549
20	0.423	0.537
21	0.413	0.526
22	0.404	0.515
23	0.396	0.505
24	0.388	0.496
25	0.381	0.487
30	0.349	0.449
35	0.325	0.418
40	0.304	0.393
45	0.288	0.372
50	0.273	0.354
60	0.250	0.325
70	0.232	0.302
80	0.217	0.283
90	0.205	0.267
100	0.195	0.254
125	0.174	0.228
150	0.159	0.208
200	0.138	0.181
300	0.113	0.148
400	0.098	0.128
500	0.088	0.115

$\rho_{crit} = 0.388$ for $\alpha = 5\%$

$\rho_{crit} = 0.496$ for $\alpha = 1\%$

The results of the analysis are shown in Table 4.9.

Sampling and analysis for total dissolved solids (TDS) has the highest priority. However, due to the high correlation coefficient between TDS and conductivity, one of the analyses can be eliminated. Total coliforms have the second highest priority. But since the correlation coefficient between total coliforms and fecal coliforms is high, analyzing for fecal coliforms is not necessary. There is also high correlation in the group BOD, COD, and TOC, thus one or two memebers can be eliminated or reduced. It can be also seen that turbidity can replace analysis for suspended solids. One can also eliminate at least one analysis from the group acidity, alkalinity, and pH and from the group hardness, coliform and alkalinity. Metals such as iron, lead, etc., have relatively low priority and at least one or more parameters from this group can be reduced. Thus, the following streamlined program could be proposed:

Parameter	Priority of sampling
pH	high
TOC or COD	high
BOD	reduced
TKN	high
Phosphates	reduced
Conductivity or TDS	high
Suspended solids or turbidity	high
Lead	reduced or not necessary
Mercury	reduced or not necessary
Iron	reduced
Copper	reduced or not necessary
Alkalinity	reduced
Hardness	reduced
Total coliforms	high
Fecal coliforms	reduced or not necessary

Sampling for other parameters of the original 22 is not necessary.

Table 4.9. CORRELATION MATRIX OF COEFFICIENT, ρ_{xy}

Parameter	pH	TOC	COD	BOD_5	TKN	P	Cond	TDS	SS	T	Pb	Hg	Fe	Cu	Alk	Ac	Ca	Hard	Mg	TC	FC	Cl
pH	--																					
TOC	0	--																				
COD	0	0.8	--																			
BOD_5	0	0.68	0.63	--																		
TKN	0	0	0.15	0.18	--																	
Phosp	0	0	0.18	0.21	0.69	--																
Conduct	0	0.30	0.41	0.35	0.33	0.17	--															
TDS	0	0.25	0.35	0.48	0.41	0.20	0.91	--														
SS	0	0.25	0.40	0.38	0.25	0.75	0.10	0.18	--													
Turb	0	0.4	0.51	0.33	0.18	0.68	0.18	0.59	0.89	--												
Pb	0.18	0	0	0	0	0	0.28	0.31	0.18	0.15	--											
Hg	0	0	0	0	0	0	0.30	0.23	0.25	0.31	0.70	--										
Fe	0.1	0	0	0	0	0	0.41	0.39	0.58	0.61	0.18	0.23	--									
Cu	0	0	0	0	0	0	0.30	0.25	0.31	0.25	0.69	0.59	0.41	--								
Alk	0.6	0	0	0	0	0	0.38	0.41	0	0	0	0	0	0	--							
Acid	0.6	0	0	0	0	0	0.20	0.15	0	0	0	0	0	0	0.49	--						
Ca	0	0	0	0	0	0	0.31	0.35	0	0	0	0	0	0	0.65	0	--					
Hard	0.1	0	0	0	0	0	0.61	0.68	0	0	0	0	0	0	0.61	0.18	0.88	--				
Mg	0	0	0	0	0	0	0.40	0.31	0	0	0	0	0	0	0.18	0	0.35	0.18	--			
T. Coli	0	0.31	0.35	0.38	0	0	0	0	0.12	0.11	0	0	0	0	0	0	0	0	0	--		
F. Coli	0	0.10	0.18	0.21	0	0	0	0	0.11	0.08	0	0	0	0	0	0	0	0	0	0.79	--	
Chlor	0	0	0	0	0	0	0.58	0.88	0	0	0	0	0	0	0	0	0	0	0	0	0	--

0 = no engineering relevance; assumed no relation.

4.5 IN-PLANT SAMPLING AND NETWORK MONITORING

If the sampling location has not been predetermined, there are statistical and other systematic methods of determining the location of sampling points. However, these methods are only tools to aid sampling personnel and do not replace the judgment and experience of the personnel.

4.5.1 Segmentation - Priority Technique

This technique can be applied to any large flowing network including an industrial plant collection system, a municipal sewerage system, or even a watershed network. To apply this technique the following information must be known:

1. The mass flow rate of the parameter of interest, $(Q_{wj}\ C_{wj})$.

2. The range of variation of the parameter input

$$p_j = (Q_{wj}\ C_{wj})\ \max - (Q_{wj}\ C_{wj})\ \min$$

3. The approximate frequency of the fluctuations, p_j.

4. Values for the coefficient of transformation through each segment, β_{AB}.

5. Values for the reduction in variation through each segment, α_{AB}.

4.5.1.1 Discussion of Methods - Segmentation of the system is done first by isolating the locations which modify the waste stream condition, e.g., junctions of wastewater treatment units, overflows, stormwater inflow, sidestreams, lateral sewers, etc. An example of a municipal wastewater system segmentation is shown in Figure 4.15. The system has 16 segments, 12 inside the waste system, 4 on the receiving water body. In an ideal but unrealistic situation one can locate sampling stations in all segments of the system. With limited economical resources, the number of sampling points will, of course, be limited. Therefore, there is a necessity for a measure to establish priorities of sampling for each segment. The measure can be the cross-correlation coefficient between the two segments. If a high correlation exists for the measured parameter between two segments, one can rely on measurement of the parameter in only one segment and sampling of the other segment is not necessary. Unlike the large river monitoring systems, wastewater systems have at least one fixed location of a monitoring point, such as the influent and/or effluent of a treatment plant. Using the cross-correlation analysis between the monitored segment and other upstream and downstream segments

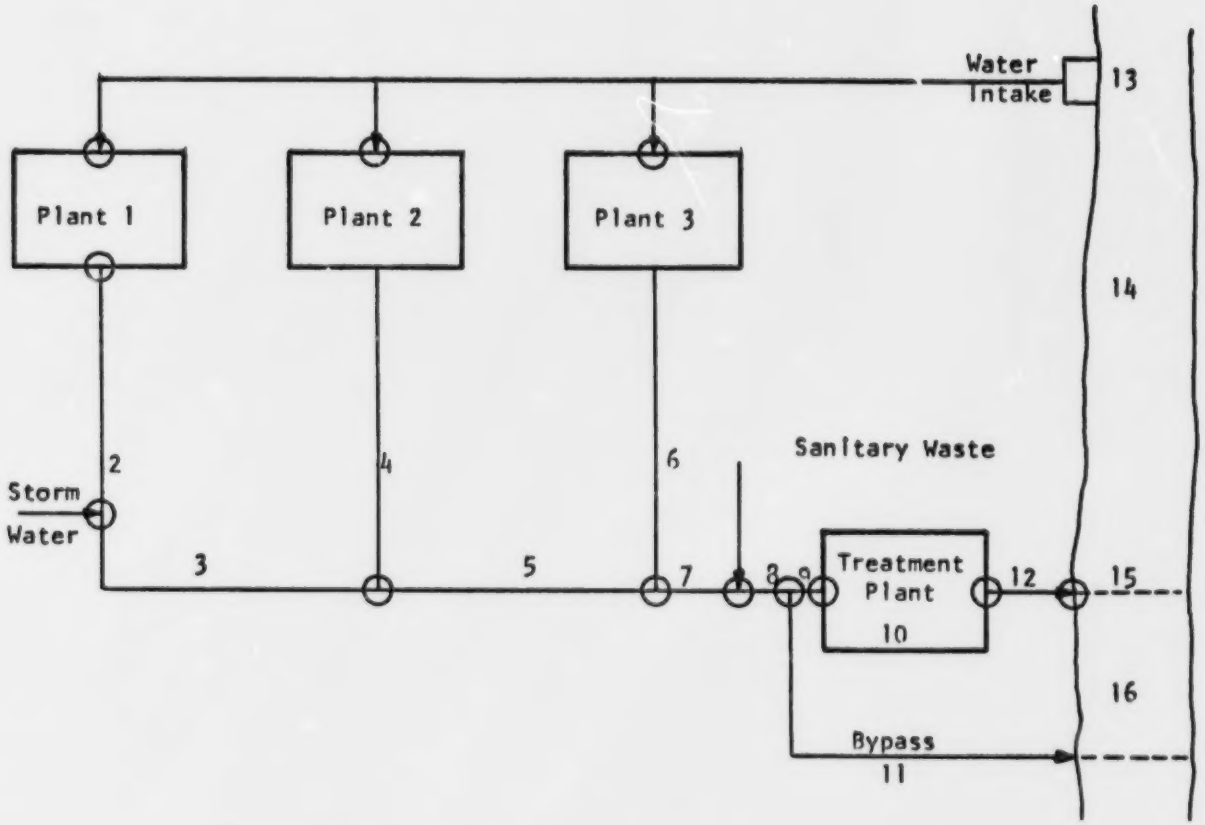


Figure 4.15. Segmentation of a wastewater system

it is possible to determine segments with low correlation to the monitored segment. A second consideration should be the worth of the data measured at the segment. For example, if the magnitude of a measured parameter and the magnitude of its variability is insignificant when related to other segments, the segment will have a low priority for monitoring.

First Priority Sampling Points - The location of at least one sampling point is strictly determined by the basic objectives of a monitoring program, i.e., protection of the environment. This objective requires that a sampling point be located just before a wastewater discharge to a receiving water body. If the industry has several wastewater outfalls, a sampling point should be located downstream from the last outfall. In the case that the monitoring point is located in the receiving water body, an upstream station to monitor the upstream water quality and quantity is necessary. This will allow the effect of the wastewater discharge on the receiving water body to be clearly identified. If the water intake for the industry is situated on the same water body, the upstream sampling point can be conveniently located at the water intake.

Second Priority Sampling Points - Other important objectives of a sampling program can be to monitor the quality of raw wastewater and to evaluate the efficiency of a treatment process. Thus, a location for a second priority sampling point would normally be at the influent to a treatment plant.

For small and middle size wastewater systems, sampling at the first and second priority sampling points should be sufficient to meet most of the objectives and requirements established by regulatory agencies.

Third Priority Sampling Points - The location of additional sampling points or sampling sites may be necessary for large wastewater systems with many inputs. Their purpose is to provide additional information or warning. In this case, the method of segmenting the wastewater system and determining sampling priorities for each segment can be of use in establishing additional sampling points. Segmentation of a wastewater system is accomplished by isolating the locations which substantially modify the waste stream conditions. These features include junctions of wastewater streams, treatment units, wastewater overflow, flow dividers, storm, and cooling water inflows, storage reservoirs, etc. A method of segmentation is outlined in the following paragraphs.

1. It is recommended that a linear graph technique be utilized to represent the wastewater system. Such a linear graph would consist of nodes and junctions and branches or lines. All wastewater inputs will enter the system through the nodes and the nodes will also separate the branches with different characteristics. A branch is considered as a segment with uniform geometric, hydraulic and

transform characteristics. The following depicts the classification of some typical elements of a wastewater system.

Nodes - manholes, change of slope, change of diameter of conduits, flow dividers, junctions of sewers and channels, outfalls, influent and effluent to treatment steps, etc.

Branches - conduits, channels, treatment steps, by-pass, adjacent receiving water bodies, storage reservoirs, holding ponds, etc.

For the industrial water/wastewater system of Figure 4.16 a linear graph representation is shown in Figure 4.17.

2. In segregating the system, each node should be uniquely numbered. Wastewater input to each node should be characterized by the range of variation

$$P_j = (Q_{wj}\ C_{wj})_{max} - (Q_{wj}\ C_{wj})_{min}$$

which is, basically, the range of waste loads to the node j. The units of P_j will be g/sec if the flow Q_w is expressed in m^3/sec and concentration, c_w in mg/l ([g/sec] = [m^3/sec] * [mg/l]). It might be convenient also to know the approximate frequency of fluctuations of the input P_j. A node table such as is shown on Table 4.10 should be prepared.

3. Each branch is identified by a double identification subscript AB where A is the number of the upstream node and B is the number of the downstream node.

Coefficients of transformation, β_{AB} and α_{AB} should be assigned for each branch. The coefficient of transformation, β_{AB}, describes roughly how the variability of the wastewater is reduced in the segment. In most cases, the coefficient of transformation, β_{AB}, can be determined approximately from the geometry of the segment and treatment parameters. The coefficient, α_{AB} describes how the correlation is reduced in the segment. The following values of the coefficients are recommended:

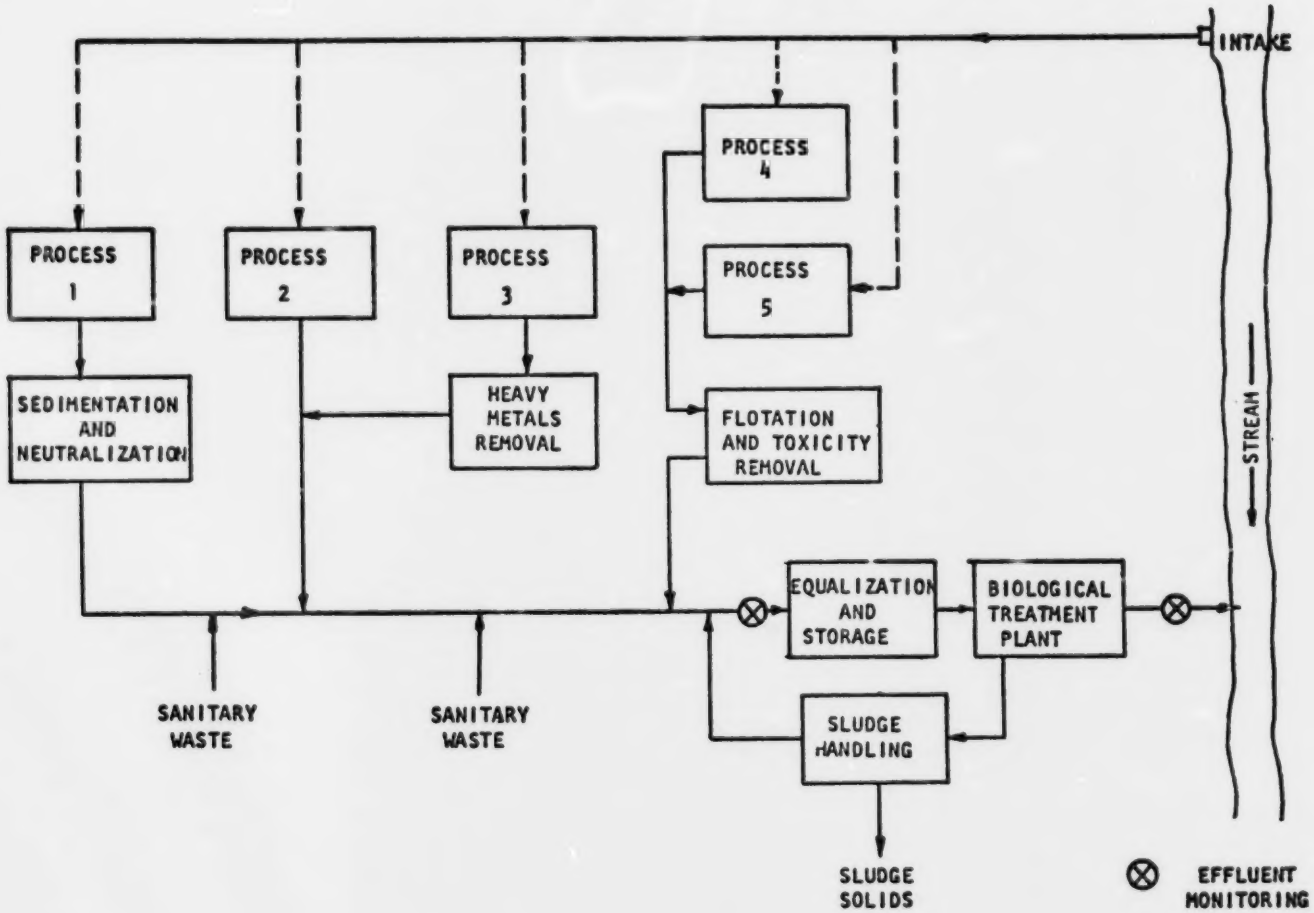


Figure 4.16. An industrial water/wastewater system

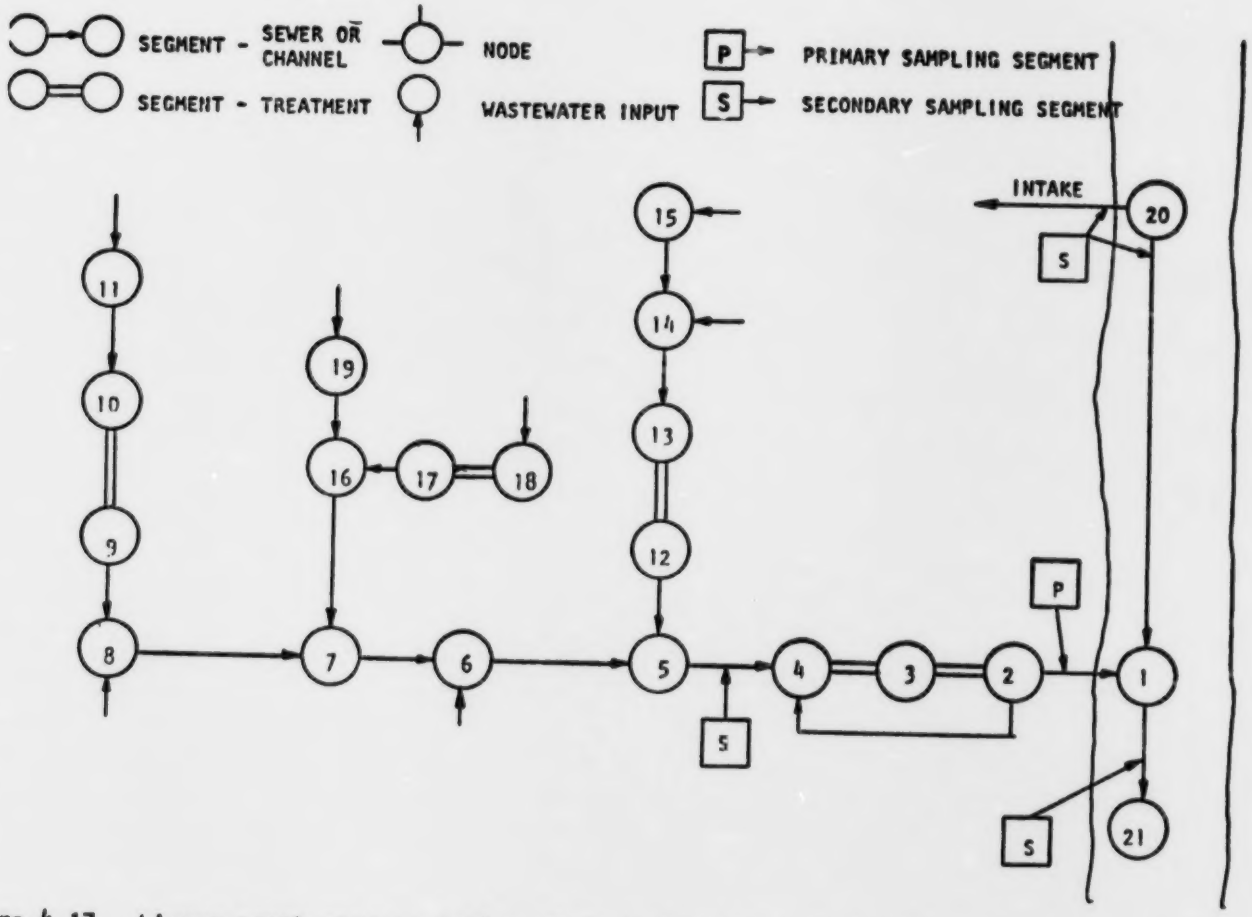


Figure 4.17. Linear graph representation of an industrial water/wastewater system

	β_{AB}	α_{AB}
Short sewers and channels	1.0	1.0
Plug flow treatment steps, long sewers and channels with decay	e^{-Kt}	0.9-1.0
Completely mixed treatment steps with short detention time ($t << 1/f$)	$1-E_{tr}/100$	0.85-0.95
Completely mixed treatment steps with long detention time ($t >> 1/f$)	$\frac{1}{\sqrt{2(1+Kt)tf}}$	$\frac{1}{\sqrt{2tf}}$
Storage and equalization reservoirs and holding ponds with no decay	$\frac{1}{\sqrt{2tf}}$	$\frac{1}{\sqrt{2tf}}$

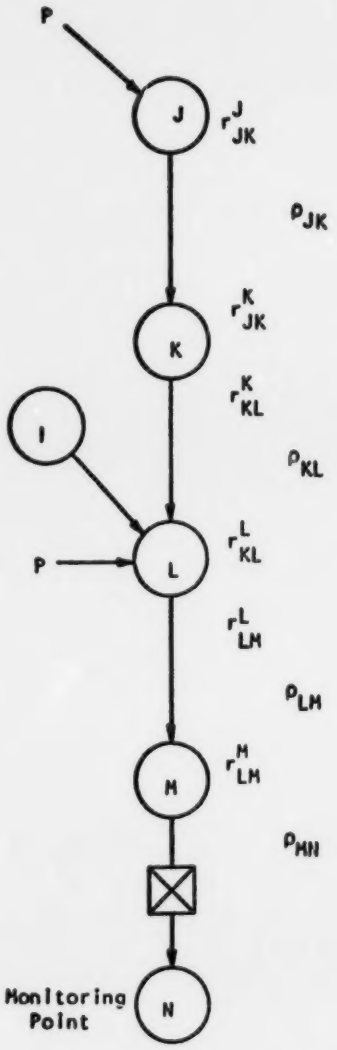
AB = double identification subscript
K = decay coefficient in the segment (base e), day^{-1}
t = detention time in the segment, days
f = frequency of fluctuations of waste inputs
E_{tr} = treatment efficiency in percent

4. Determine approximate ranges of wastewater quality variations for each segment. This can be done approximately by starting at the most upstream nodes containing wastewater inputs and moving downstream. The variability will be modified by mixing downstream, by the buffering capacity of segments, and by new wastewater inputs (such as process discharges) in downstream nodes.

   Figure 4.18 illustrates how this procedure is accomplished. JK is the most upstream node containing a wastewater input and would therefore be the starting point. The range of wastewater variability will be:

$$r^J_{JK} = P_j$$

   where r^J_{JK} is the wastewater quality variation range in segment JK downstream from J. Above the downstream node K the variation range becomes:



Variability Range

$$r^J_{JK} = P$$

$$r^K_{JK} = r^J_{JK} * \beta_{JK}$$

$$r^K_{KL} = r^K_{JK}$$

$$r^L_{KL} = r^K_{KL} * \beta_{KL}$$

$$r^L_{LM} = \sqrt{(r^L_{KL})^2 + (r^L_{IL})^2 + (P_L)^2}$$

$$r^M_{LM} = r^L_{LM} * \beta_{LM}$$

Figure 4.18. Estimation of variability and correlation in segments

$$r^K_{JK} = r^J_{JK} * \beta_{JK}$$

At a node the variability range can be changed by wastewater inputs to the node and by other upstream branches entering the node. For a case where more than one input enters a node, the following relationship (Propagation of Errors) can be used to compute the variability range:

$$r^A_{AB} = \sqrt{\sum_i (r^A_{iA})^2 + \sum_j (P_{ja})^2}$$

Where A denotes the node under consideration, B denotes a node immediately downstream from A, iA represents the upstream branches entering node A, and P_{jA} represents the wastewater inputs entering node A. In Figure 4.17, the above formula is used for node L.

The variability ranges for all segments in a network can be computed using the relationships described above and shown on Figure 4.18. It is recommended that the variability range be checked by known data from a survey or monitoring. The above procedure should give adequate results assuming that all inputs to the system are random and uncorrelated to each other.

5. Determine the approximate correlation coefficient for each segment's water quality variations related to the variations in the monitored segment. The correlation coefficient for the monitored segment, ρ_{MN}, itself equals of course 1.0. Moving further downstream or upstream the correlation coefficient will decrease as the relation between the wastewater fluctuations in the monitored segment and the segment downstream or upstream diminishes. The change of the correlation coefficient can be roughly estimated as follows:

   <u>In a Branch</u>: multiply the ρ by coefficient α

   <u>In a Node</u>: multiply the correlation coefficient by the ratio:

$$\frac{r^{B}_{AB}}{r^{B}_{BC}}$$

where B is the node under consideration, AB is the branch located further away from the monitored segment, and BC is the branch located closest to the monitored segment.

6. Additional sampling points should be located at the segment where theoretically, the correlation influence of the monitored point ends. Since the correlation influence of both points extends both downstream and upstream there will be an overlap such that each sampling point will have an area of influence to $\rho = \sqrt{\rho_c}$ where ρ_c is the correlation level on which the hypothesis of the existence of a correlation between two water quality records is denied. Table 4.8 gives the values of the critical coefficient of correlation, ρ_c. If the number of samples is not known, a value of $\rho_c = 0.25 - 0.30$ will give a good estimate.

7. If there are several segments to be monitored, i.e., one or more segments have a correlation level less than the critical ρ_c, the priority can be determined according to the magnitude of the variability range r_{ij} for the segment ij. The segment with the highest r_{ij} will have the highest priority.

8. Once a new sampling location is established, the procedure shall be repeated to find the next sampling location.

9. This procedure should also be repeated for each important parameter.

4.5.1.2 Example of Segmentation Technique

Determine the location of sampling points for the wastewater system given in Figure 4.16. The analysis will be based on the COD information representing the organic load to the system.

Step 1 - Divide the system into segments such as on the linear graph representation in Figure 4.17.

Step 2 - Locate a first priority sampling point (P) at the effluent channel (segment 1-2). Locate second priority sampling points (S) at the influent to the treatment plant (segment 4-5) and in the receiving water body (upstream and downstream from the waste discharge).

Step 3 - Estimate the variability range of the inputs to the system (Table 4.10)

Step 4 - Estimate the coefficients of variation β and α for each segment (Table 4.11).

Step 5 - Estimate the variation range in each segment. Proceed from the most downstream and work upstream (Table 4.12 left portion).

Step 6 - Estimate the coefficient of correlation of wastewater variations in each segment as related to the nearest monitored segment, i.e., to the segment 4-5. Proceed from the monitored segment ($\rho = 1.0$) and work upstream (Table 4.12 right portion). Each segment is correlated to the segment immediately downstream toward the monitoring point.

At this stage developing a correlograph (Figure 4.19) will aid in the decision process in Step 7.

Step 7 - Once the correlation coefficients are estimated find those where $\rho < \rho_c$, with ρ_c estimated to be 0.30. Based on this criterion the priority for monitoring should be in segments 17-18, 16-17, 14-15, 13-14, 12-13, 16-19. However, when one segment is chosen for monitoring, the upstream and downstream segments will usually have a high correlation and, therefore, only one segment needs to be monitored. The second criterion is the magnitude of the variability, r_{ij}, for the segments with low correlation levels. Both the ρ and r_{ij} values should be examined for these segments, the requirements and objectives of the program should be considered, and then professional judgment must be excercised.

In this example segments 17-18, 16-17, and 16-19 are neighboring segments with low correlation levels. Looking at the variability values, segment 16-19 has the highest value, indicating the greatest fluctuations in wastewater quality. Therefore, of these three, segment 16-19 might have the highest priority. Segments 14-15, 13-14, and 12-13 are also neighboring segments with low correlation levels. Segment 13-14 has the greatest variability and therefore would be chosen of the three. Since its variability is much higher than that for segment 16-19, it would have the highest overall priority. At this stage correlation and variability values can be recalculated to see if monitoring at these points would satisfy the program requirements. If not, the procedure should be repeated.

Table 4.10. WASTEWATER LOADS TO NODES

CONSTITUENT: COD

Node	Maximal Loading g/sec	Minimal Loading g/sec	PJ
1	0	0	0
2	0	0	0
3	0	0	0
4			
5	0	0	0
6	10	1.2	8.8
7	0	0	0
8	30.0	6.0	24.0
9	0	0	0
10	0	0	0
11	175	100	75
12	0	0	0
13	0	0	0
14	66.0	17.0	49.0
15	109	21.0	88.0
16	0	0	0
17	0	0	0
18	42	23	19
19	121.50	93.0	28.5

Fluctuations of maximum and minimum at most nodes - 1/8 hrs^{-1}

Table 4.11. COEFFICIENTS OF VARIATION IN BRANCHES

Branch	Description	β	α
1-2	Effluent Channel	1.0	1.0
2-3	Activated Sludge Plant	0.1	0.4
3-4	Equalization Basin	0.2	0.2
4-5	Sewer	1.0	1.0
5-6	Sewer	1.0	1.0
6-7	Sewer	1.0	1.0
7-8	Sewer	1.0	1.0
8-9	Sewer	1.0	1.0
9-10	Neutralization Plant	0.9	0.9
10-11	Sewer	1.0	1.0
5-12	Sewer	1.0	1.0
12-13	Flotation Unit	0.5	0.5
13-14	Sewer	1.0	1.0
14-15	Sewer	1.0	1.0
7-16	Sewer	1.0	1.0
16-17	Sewer	1.0	1.0
17-18	Chemical Coagulation	0.7	0.7
16-19	Sewer	1.0	1.0

Table 4.12. DETERMINATION OF THE SAMPLING PRIORITIES OF SEGMENTS

Segment	Upstream variation range $r_u = (\Sigma r^2 + \Sigma p^2)^{0.5}$	Downstream variation range $r_d = r_u * \beta$	Correlation coefficient at the downstream node $\rho_u = \rho_d \frac{u}{r_d}$	Correlation coefficient in the branch at the upstream node $\rho = \rho \alpha$	Priority for tertiary monitoring
16-19	28.5	28.5	0.33 * 28.51/31.45 = 0.30	0.30	T2
17-18	19.0	19 * 0.7 = 13.3	0.14	0.14 * 0.7 = 0.10	T3
16-17	13.3	13.3	0.33 * 13.3/31.45 = 0.14	0.14	
7-16	$(28.5^2 + 13.3^2)^{0.5} = 31.45$	31.45	0.81 * 31.45/78.24 = 0.33	0.33	
10-11	75	75	0.63	0.63	
9-10	75	75 * 0.9 = 67.5	0.70	0.7 * 0.9 = 0.63	
8-9	67.5	67.5	0.75 * $\frac{67.5}{71.64}$ = 0.70	0.70	
7-8	$(67.5^2 + 24^2)^{0.5} = 71.64$	71.64	0.81 * 71.64/78.24 = 0.75	0.75	
6-7	$(71.64^2 + 31.45^2)^{0.5} = 78.24$	78.24	0.82 * 78.24/78.73 = 0.81	0.81	
5-6	$(78.24^2 + 8.8^2)^{0.5} = 78.73$	78.73	1.0 * 78.73/96.12 = 0.82	0.82	
14-15	88.0	88.0	0.26 * 88/100.72 = 0.23	0.23	
13-14	$(88^2 + 49^2)^{0.5} = 100.72$	100.72	0.26	0.26	T1
12-13	100.72	100.72 * 0.5 = 50.36	0.52	0.52 * 0.5 = 0.26	
5-12	50.36	50.36	1.0 * 50.36/46.12 = 0.52	0.52	
4-5	$(78.73^2 + 50.36^2)^{0.5} = 96.12$	96.12	1.0	1.0	Initial segment monitoring

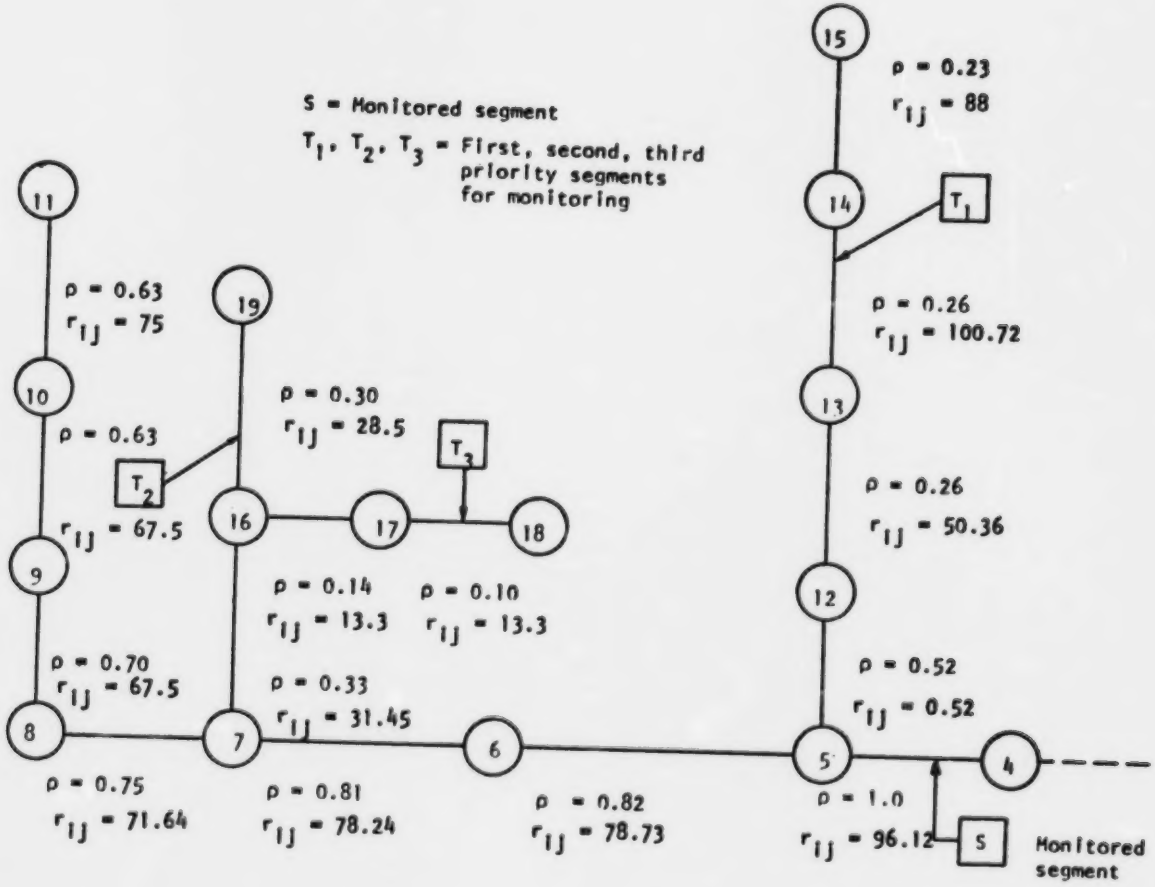


Figure 4.19. Correlograph for segments

4.5.2 Probability of Exceeding a Standard

In locating sampling points in a receiving water body the probability of exceeding a receiving water standard should be considered. For all conservative substances and all non-conservative substances except oxygen and possibly temperature and nitrates, the critical section would be located immediately downstream from the outfall. The section with the maximum probability of violating the dissolved oxygen standard will be further downstream near the "sag-point". The location of the critical point can be approximately evaluated as follows (14):

The probability that the dissolved oxygen standard will be exceeded is:

$$p(C < C_s) = p\ (D > D_s) = \frac{1}{\sqrt{2\pi}} \int_Z^{\infty} \exp\left(-\frac{Z^2}{2}\right) dZ$$

$$\text{where } Z = \frac{D_S - \bar{D}\ (x)}{S_D(x)}$$

and C = dissolved oxygen concentration

C_s = dissolved oxygen standard

D = oxygen deficit

D_s = maximal allowable oxygen deficit

$\bar{D}\ (x)$ = average oxygen deficit at distance x from the outfall

$S_D\ (x)$ = standard deviation of the deficit at the distance x

It can be seen that to find a maximal $p(C < C_s)$ it is sufficient to find min Z or to find a location x where

$$\frac{D_s - \bar{D}(x)}{S_D(x)} = \min\ (Z)$$

The average dissolved oxygen can be computed from the equation

$$\bar{D}\ (x) = \frac{K_1 \bar{L}_o}{K_2 - K_1} \left(e^{-K_1 \frac{X}{U}} - e^{-K_2 \frac{X}{U}}\right) + D_o\, e^{-K_2 \frac{X}{U}}$$

where $\bar{L}_o$ = average BOD discharge

K_1 = coefficient of deoxygenation

K_2 = coefficient of reaeration

D_o = initial oxygen deficit

U = stream velocity

The standard deviation of the oxygen fluctuation can be related to the fluctuation of the BOD discharge as follows (14, 15, 16):

$$S_D(x) = A_1 * (UX) * S_{L_o}$$

where

$$A_1 = \frac{K_1}{K_2 - K_1} \left(e^{-K_2 \frac{X}{U}} - e^{-K_1 \frac{X}{U}} \right)$$

S_{L_o} = standard deviation of the BOD discharge

Since D_S is a given constant the conditions satisfactory for finding x with max p $(D(x) > D_S)$ is

$$\left. \frac{\bar{D}(x)}{S_D(x)} \right|_{x_{max}} = \max \frac{\bar{D}(x)}{S_D(x)}$$

The distance x_{max} can be found by plotting $\frac{\bar{D}(x)}{S_D(x)}$ vs. x for given

K_1, K_2, D_o, L_o, and U.

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```
C  PROGRAM AUTO-STATISTICS
C ************************************
C COMPUTES AUTOCORRELATIONS AND AUTOSPECTRA
C ********************************************
      DIMENSION X(1000,10),XM(10),VAR(10),ACOV(150,10),W(10
     P0),SPEC(150,10)
      READ(5,10) NS,N,MAXM,DELTA
      WRITE(6,70) NS,N,MAXM,DELTA
   70 FORMAT(3I5,F11.6)
C ************************************************************
C NS= NO OF X SERIES
C N = NO OF VALUES IN A SERIES
C MAXM= MAX LAGS NO
C DELTA = TIME INCREMENT
C ************************************************************
      DO 60 I=1,N
      READ(5,11)(X(I,J),J=1,NS)
C*************************************************
CX(I=1,N;J=1,NS)IS ARRAY OF DATA
C*************************************************
   60 CONTINUE
      DO 20 J=1,NS
      XM(J)=0
      DO 21 I=1,N
      XM(J)= XM(J)+X(I,J)
   21 CONTINUE
      XM(J)=XM(J)/N
   20 CONTINUE
C ************************************
C VARIANCE COMPUTATION
C ************************************
      DO 22 J=1,NS
      VAR(J)=0
      DO 23 I=1,N
      X(I,J)=X(I,J)-XM(J)
      VAR(J)=X(I,J)**2+VAR(J)
   23 CONTINUE
      VAR(J)=VAR(J)/(N-1)
   22 CONTINUE
      WRITE(6,12)
      WRITE(6,13)
      DO 24 J=1,NS
      WRITE(6,14) J,XM(J),VAR(J)
   24 CONTINUE
   10 FORMAT(3I5,F10.4)
   11 FORMAT(10F10.0)
12    FORMAT(23HSERIES AVERAGE VARIANCE)
13    FORMAT(40H****************************************)
   14 FORMAT(I3,F13.4,F15.2)
```

Figure 4.20. Spectral analysis computer program

```
C ***********************
C AUTOCORRELATION
C ***********************
      MAXL=MAXM+1
      DO 34 J=1,NS
      DO 35 I=1,MAXL
      ACOV(I,J)=0
   35 CONTINUE
   34 CONTINUE
      DO 26 J=1,NS
      DO 27 IP=1,MAXL
      K=IP-1
      NP=N-K
      DO 28 I=1,NP
      IK=I+K
      ACOV(IP,J)=ACOV(IP,J)+X(I,J)*X(IK,J)
   28 CONTINUE
      ACOV(IP,J)=ACOV(IP,J)/NP
   27 CONTINUE
   26 CONTINUE
      WRITE(6,15)
      WRITE(6,16)
      DO 29 I=1,MAXL
      DO 80 J=1,NS
      W(J)=ACOV(I,J)/ACOV(1,J)
   80 CONTINUE
      K=I-1
      AD=K*DELTA
      WRITE(6,17)AD,(W(J),J=1,NS)
   29 CONTINUE
15    FORMAT(39H    LAG TIME            AUTOCORRELATIONS)
16    FORMAT(100(1H=))
   17 FORMAT(F5.1,(10F13.2))
C ***********************************
C  AUTOSPECTRUM
C ******************************
      NF=2*MAXM
      MAXL=MAXM-1
      DO 43 J=1,NS
      DO 40 K=1,MAXL
      RK=K
       W(K)=0.5*(1+COS(3.14157*RK/MAXM))
   40 CONTINUE
      NP=NF+1
      DO 42 I=1,NP
      IX=I-1
      SPEC(I,J)=0.0
      DO 41 K=1,MAXL
      RK=K
      KZ=K+1
      SPEC(I,J)=SPEC(I,J)+ACOV(KZ,J)*W(K)*COS(3.14157*RK*IX/NF)
   41 CONTINUE
      SPEC(I,J)=2*DELTA*(ACOV(1,J)+2*SPEC(I,J))
   42 CONTINUE
   43 CONTINUE
      WRITE(6,18)
      WRITE(6,19)
      DO 44 I=1,NP
      IX=I-1
      FREQ=IX/(2.0*DELTA*NF)
      WRITE(6,50) IX,FREQ,(SPEC(I,J),J=1,NS)
   44 CONTINUE
18    FORMAT(41HLAG NO  FREQUENCY              AUTOSPECTRA)
19    FORMAT(100(1H=))
50    FORMAT(I5,3X,F11.6,2X,(10F14.3))
      STOP
      END
*
```

Figure 4.20 (Continued). Spectral analysis computer program

CHAPTER 5

SAMPLING MUNICIPAL WASTEWATERS

5.1 BACKGROUND

Municipal wastewater consisting of the spent waters from a community is treated by chemical, physical, or biological means prior to discharge to surface waters. Three stages of treatment are commonly used at municipal treatment plants (1): primary (screening, sedimentation), secondary (activated sludge, trickling filter etc.), and tertiary (physical/chemical treatment). The wastewater characteristics vary with the size and habits of the community, the type of collection system (combined or separate), the amount of infiltration, and the type of industrial discharges.

5.2 OBJECTIVES OF SAMPLING PROGRAMS

5.2.1 Regulatory

Sampling of municipal wastewaters is required by regulatory agencies for the NPDES permit program (2). The location of sampling points, frequency, sample type, etc. are specified in the permit.

5.2.2 Process Control

In addition, sampling is performed at municipal treatment plants for process control purposes. This monitoring provides a check on the efficiency of the process allowing the operator to make adjustments to optimize the process efficiency.

5.2.3 Research

The special needs of a research project will dictate the sampling program. Hence each project must be considered individually and no general guidelines can be given.

5.3 FREQUENCY OF SAMPLING

5.3.1 Established by Regulation

Follow the frequency requirements indicated in the permit issued by the regulatory agencies.

5.3.2 Use of Statistics

Apply spectral analysis techniques (Section 4.3.2) to establish the optimum frequency. If the data required for this technique is not available:

1. Conduct a week-long survey collecting hourly samples. (Choose a week of high industrial production).

2. Determine if any unusual industrial or community discharge occurred during the sampling period (e.g. an extensive spill or extremely heavy rainstorm) which may invalidate the data and necessitate a repeated survey.

After data collection, the analysis of data should be performed as outlined previously.

5.3.3 Surveillance Purposes

A poll of EPA Surveillance and Analysis Labs indicated a general concurrence that for normally variable domestic wastewaters a minimum of 8 evenly-spaced grab samples collected over a 24 hour period, repeated for a minimum of 3 weekdays, will result in a fair estimate of water chemistry characteristics (3).

5.3.4 Other Considerations

Follow interim sampling frequencies prior to the generation of data for statistical analysis. Frequencies appear in Tables 5.1 and 5.2.

5.4 LOCATION OF SAMPLING POINTS

5.4.1 Effluent Monitoring

Use effluent monitoring points established by regulatory permits. Sample the effluent in a combined effluent pipe or mixing chamber and avoid accumulated grease and oil. For BOD analysis, it is recommended that samples be collected prior to the disinfection step because of severe problems associated with the BOD test for disinfected effluents (4). When manually compositing effluent samples according to flow and when an effluent flow measuring device is not available, use the influent flow measurement without any correction for time lag. The error between the influent and effluent flow measurement is insignificant except in those cases where large volumes of water are impounded (such as in reservoirs) as a result of influent surges coupled with highly restrictive effluent discharge (5).

Table 5.1. PROCESS TESTING GUIDE[a] (From 6)

PROCESS	TEST	FREQUENCY
	PRETREATMENT	
Grit Removal	Volatile Solids	Daily
	Total Solids	Daily
	Moisture Content	Daily
	PRIMARY TREATMENT	
Primary Sedimentation	Settleable Solids	Daily
	pH	Daily
	Total Sulfides	Daily
	Biochemical Oxygen Demand	Weekly
	Suspended Solids	Weekly
	Chemical Oxygen Demand	Weekly
	Dissolved Oxygen	Weekly
	Grease	Weekly
	SECONDARY TREATMENT	
Activated Sludge	Suspended Solids	Daily
	Dissolved Oxygen	Daily
	Volatile Suspended Solids	Weekly
	Turbidity	Daily
Trickling Filter	Suspended Solids	Daily
	Dissolved Oxygen	Daily
Oxidation Ponds	Dissolved Oxygen	Daily
	Total Sulfides	Daily
	Total Organic Carbon	Weekly
	Total Phosphorus	Weekly
	Settleable Solids	Daily
	pH	Daily
	Total Sulfides	Daily
Final Sedimentation	Biochemical Oxygen Demand	Weekly
	Suspended Solids	Weekly
	Chemical Oxygen Demand	Weekly
	Dissolved Oxygen	Weekly
	Turbidity	Daily
	MBAS	Weekly

[a] This is a minimum sampling guide, and is subject to change with plant site, complexity of operation, and problems encountered.

Tab'e 5.1. (Continued)
PROCESS TESTING GUIDE[a] (From 6)

PROCESS	TEST	FREQUENCY
	DISINFECTION	
Chlorination	Chlorine Residual	Daily
	MPN Coliform	Weekly
	SOLIDS HANDLING	
Thickening	Suspended Solids	Daily
	Volatile Solids	Daily
Digestion	Total Solids	Weekly
	Volatile Solids	Weekly
	pH	Daily
	Gas Analysis	Weekly
	Alkalinity	Weekly
	Volatile Acid	Weekly
Centrifuging	Suspended Solids	When in Operation
	Volatile Solids	When in Operation
Vacuum Filters	Sludge Filterability	When in Operation
	Suspended Solids	When in Operation
	Volatile Solids	When in Operation
Incineration	Ash Analysis	When in Operation
	ADVANCED TREATMENT	
Chemical Coagulation & Flocculation	Jar Test	Weekly
	Phosphorus Analysis	Weekly
Activated Carbon	Apparent Density	Weekly
	COD	Weekly
	TOC	Weekly
Recarbonation	pH	Weekly
Ammonia Stripping	Ammonia Nitrogen	Weekly
	pH	Weekly
Filters	Suspended Solids	Daily
	Turbidity	Daily
Microscreen	Suspended Solids	Daily
	Chemical Oxygen Demand	Weekly

[a] This is a minimum sampling guide, and is subject to change with plant site, complexity of operation, and problems encountered.

Table 5.2. RECOMMENDED MINIMUM SAMPLING PROGRAMS FOR MUNICIPAL WASTEWATER TREATMENT PROCESSES (From 7)

	Overall		Grit Removal		Primary Clarification		Activated Sludge		Trickling Filter		Aerated Pond		Secondary Ponds		Secondary Clarifier		Chlorine Contact		Chemical Treatment		Nitrogen Removal		Two Stage Recarbon		Filtration		Activated Carbon		Centrifugation		Sludge Concentration		Solids Reduction		Solids Reduction	
	S[1]	F[2]	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F
Temp	G	1/D									G	1/D	G	1/N			G	1/D			G	3/D											G	1/D	Mo	
pH	G	1/D					G	5/N			G	3/N	G	1/N	G	1/D	G	1/D	G	1/D or Mo	G	3/D	Mo				Mo						G	1/D	G	1/D
BOD	C	2/N			C	2/N	C	2/N	C	2/N					C	2/N									G	Back-wash			G	1/N	G	2/N	G	Dump	G	1/D
DO	G	3/N					G	5/N			G	1/D	G	1/N																			G	3/N		
SS	C	3/N			C	3/N	C	5/N							C	3/N			C	1/D					G	Back-wash			G	1/D	G	1/D	G	Dump	G	1/N
NH_3-N	C	1/N					C	1/D							C	1/D					C	1/N														
TKN	C	1/N					C	1/D							C	1/N					C	1/N														
NO_3-N	C	1/N					C	1/D							C	1/D					C	1/N														
P-T	C	1/N					C	3/N							C	1/D			C	3/N																
Turb	R														Mo				R						R											
TS	C	2/N	G	2/N	G	1-3/N									G	3/N			G	1-3/N			C	1/N					G	1/D	G	1/D	G	2/N	G	1/N
TVS	C	2/N	G	2/N			C	3/N																									G	2/N	G	2/N
Set. S					G	3/N									G	1/D													G	1/H			G	3/N		
Sl. Vol.																			G	3/D																
COD					C	1/N	C	2/N	C	2/N																	C	3/N								
V. SS					C	3/N																														
Air Input							R																										R			

Table 5.2 (continued). RECOMMENDED MINIMUM SAMPLING PROGRAMS FOR MUNICIPAL WASTEWATER TREATMENT PROCESSES (From 7)

	Overall		Grit Removal		Primary Clarification		Activated Sludge		Trickling Filter		Aerated Pond		Secondary Ponds		Secondary Clarifier		Chlorine Contact		Chemical Treatment		Nitrogen Removal		Two Stage Recarbon		Filtration		Activated Carbon		Centrifugation		Sludge Concentration		Solids Reduction		Aerobic Digestion		Solids Reduction		Anaerobic Digestion	
	S[1]	F[2]	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F
Micro Analysis							G	2/W																																
Ortho-P							C	3/W							C	1/D			C	3/W																				
Chlor. Resid.																	G R	1/D																						
Coliform																	G	1/W																						
Fecal Coll.																	G	1/W																						
Alk.	C	2/W													C	1/W			C	2/W			C	1/[illegible]									G	2/W			G	1/D		
Jar Test																	C	1/M																						
Hardness																	C	1/W			C	1/W																		
Sludge Vol.					G	3/D									G	3/D																								
Dis. S	C	2/M																			G	3/W	C	1/W																
MBAS																											C	1/D												
Metals	C	2/M																																						
Plant Flow		R																																						

1. S = type of sample
2. F = frequency

G = Grab
C = 24 hour composite
D = Day
W = Week
M = Month
R = Record continuously
Mo = Monitor continuously

5.4.2 In-Plant Locations

Apply the statistical technique outlined in Section 4.5.1 to determine in-plant sampling locations. In addition to these locations, sample all other unit processes periodically or when the variability of a parameter adversely affects the efficiency of a unit process.

5.5 NUMBER OF SAMPLES

Use one or more of the following methods to determine the number of samples:

1. Follow permit requirements by regulatory agencies.
2. Apply statistical methods in Section 4.2 to the data from the preliminary survey.
3. Use the frequency data to establish number of samples (e.g. 1 sample every 6 hours will establish 4 samples per day).

5.6 PARAMETERS TO MEASURE

5.6.1 NPDES Requirements

Analyze all parameters as required for the NPDES permit system.

5.6.2 Other Parameters

Monitor the following parameters routinely, regardless of plant size. (8)

1. BOD
2. Suspended Solids
3. pH
4. Flow

Secondary analyses include:

1. Fecal Coliform and Chlorine Residual
2. Temperature
3. Dissolved Oxygen
4. Total Solids
5. Total Volatile Solids
6. Nitrogen Series
7. Phosphorus
8. Dissolved Solids
9. Alkalinity
10. Metals
11. COD
12. Oil and Grease

Table 5.2 indicates the parameters to analyze for various unit processes. Changes are allowed to compensate for specific plant conditions.

5.7 TYPE OF SAMPLE

Use composite samples for all overall monitoring (9) and grab samples for checking individual unit processes. Use one of the following types of composite samples to properly estimate mass loading:

1. Continuous, volume proportional to flow

2. Periodic, volume constant, time proportional to flow since the last sample.

Other composite types may be used if comparable results can be demonstrated.

5.8 METHOD OF SAMPLING

Use automatic samplers whenever routine monitoring or process control is the objective. The inaccuracies caused by untrained personnel collecting samples must be avoided (10). If manual grab samples are necessary, allow only trained personnel who understand the importance of sampling to collect them.

5.9 AUTOMATIC SAMPLERS

Automatic samplers for municipal wastewaters must be capable of collecting representative suspended solids samples throughout the collection and treatment system. While sampler selection will depend on site conditions, the following guidelines are suggested:

1. For sampling raw wastewater and primary effluent, use a sampler having an intake velocity greater than 0.76 m/sec (2.5 ft/sec). For sampling a final effluent with no visible solids, a sampler having a lower intake velocity may be acceptable (3).

2. To determine the effectiveness of an automatic sampler to collect suspended solids, statistically compare the suspended solids values of the composite sample from the sampler with the mean value of manual grab samples, with a minimum compositing period of six hours and a maximum individual sample frequency of one hour (15). The acceptable ratio of sampler to manual grab suspended solids values varies throughout the plant: influent and primary effluent - 1.6-2.0; final effluent - 0.9-1.3 (3,11).

5.10 VOLUME OF SAMPLE AND CONTAINER TYPE

For analyzing BOD, suspended solids and pH, collect a minimum volume of 2 l (0.6 gal.) (12). Use a separate sterilized container for coliform analysis. Collect chlorine residual or oil and grease samples in a glass container. Plastic is acceptable for the other recommended analyses. Specific information by parameter type is given in Chapter 10.

5.11 PRESERVATION AND HANDLING THE SAMPLES

Follow the techniques indicated in Chapter 10 to preserve the sample. Composite samples should be iced during the compositing period.

5.12 FLOW MEASUREMENT

Establish a permanent flow measurement station at the influent to the plant (after coarse screening) if none exists. Use a Parshall flume and non-fouling secondary measurement device. Individual flow measurement to unit processes can also be monitored for process control purposes. As stated in Section 5.4.1, the flow rate of the effluent can in most cases be considered identical to the influent flow with no time lag.

5.13 REFERENCES

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CHAPTER 6

SAMPLING INDUSTRIAL WASTEWATERS

6.1 BACKGROUND

Industrial wastewaters vary in contamination, flow, frequency, and type of discharge. This chapter presents general guidelines and considerations so that effective sampling programs can be established for varied situations.

6.2 OBJECTIVES OF SAMPLING PROGRAMS

6.2.1 Regulatory

The emphasis on industrial wastewater monitoring has increased with the necessity to obtain a permit for discharging wastewater into navigable waters (1). The permittee is required to compile and maintain records of all monitoring activities as specified by the permit. Depending on the nature of the discharge, the sampling frequency and parameters may differ significantly.

6.2.2 Other Objectives

There are other reasons for industrial sampling as summarized by Black (2):

1. Determining quantities of pollutional materials discharged during a 24-hour day and per unit weight of product.

2. Locating major waste sources within the plant to permit computing of constituent balances.

3. Exploring potential recovery from a given department or unit process, considering process modifications, and studying the economics thereof.

4. Defining factors influencing character of wastes from a given department or unit process.

5. Investigating and demonstrating variations in character and concentration of combined wastes.

6. Establishing a sound basis for treatment of residual wastes.

Therefore, an effective sampling program can not only meet regulatory requirements but also reduce material losses and hazardous discharges and determine system malfunctions.

6.3 FREQUENCY OF SAMPLING

6.3.1 Established by Regulation

Use permit requirements when compliance monitoring is the objective. If the sampling frequency is not specified by regulation, use the statistical methods as discussed below.

6.3.2 Use of Statistics

Apply the statistics outlined in Section 4.3.2 to obtain frequency of sampling whenever possible. Background data must be collected to determine mean and variance. One of the following procedures can be used to obtain this information (listed in order of preference) if it has not been previously collected:

1. Conduct a week long preliminary survey consisting of the hourly samples to characterize the system.

2. Conduct one 24-hour survey taking hourly samples (as outlined in Section 2.4). Analyze individual samples if batch dumps are suspected. Any weekly pattern must be considered and samples taken on the day of the greatest variation of the parameters of interest.

3. Obtain data from a plant with the same type of industrial operation. However, where processes differ, take samples to quantify the variation.

After data collection, use production figures to determine extreme values, assuming a linear operating relationship (which is not always the case).

6.3.3 Other Considerations

Consider variable plant operations when determining frequency:

1. Seasonal operation
2. Less than 24 hour per day operation
3. Special times during the day, week or month set aside for cleanup
4. Any combination of the above.

When monitoring these types of operations, it is necessary to sample during normal working shifts in the season of productive operation. Figure 6.1 gives procedures for the various situations.

6.4 LOCATION OF SAMPLING POINTS

6.4.1 Effluent Monitoring

Regulatory permits establish effluent monitoring points within a plant. The permit may specify only the total plant discharge or a specific discharge from a certain operation or operations. Consult permits for these locations, or use those recommendations for obtaining representative samples given in Section 2.5.

6.4.2 In-Plant Locations

In-plant sample locations are necessary if process control is the objective. Use the statistical techniques outlined in Section 4.5.1 to establish the critical sampling locations within the plant. A preliminary survey may be required to determine the variability of the individual discharges. If a point of upset exists within the plant, establishment of a sampling station or monitoring equipment at that point will allow early detection.

Batch discharges may also require individual sampling stations to establish their total impact on a discharge stream.

6.5 NUMBER OF SAMPLES

There are two ways to determine the number of samples:

1. Follow requirements from permit for regulatory monitoring.
2. Apply statistical methods (Section 4.2) to data from a preliminary survey.

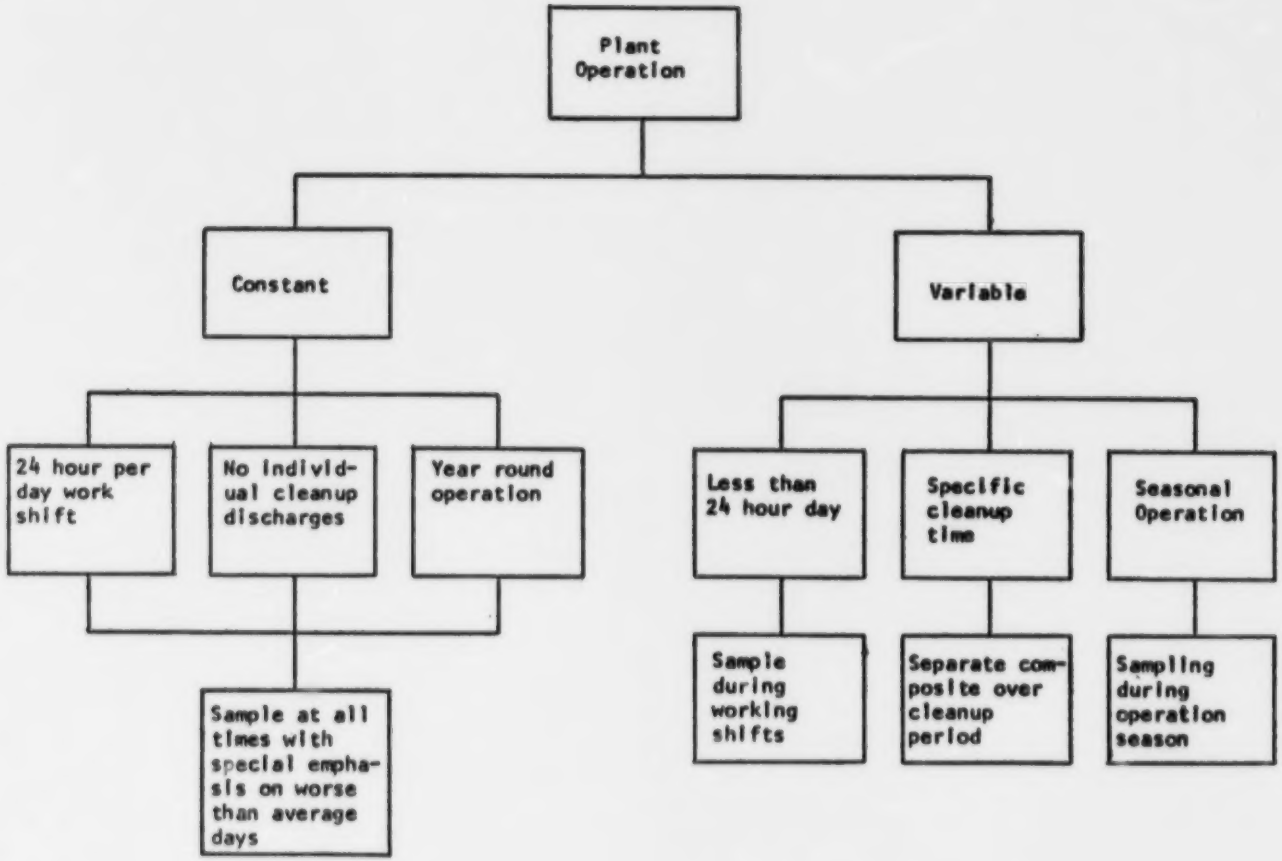


Figure 6.1. Factors of plant operation to be considered in the design of the sampling program

6.6 PARAMETERS TO MEASURE

6.6.1 NPDES Requirements

Parameters required for measurement in NPDES permits are listed by industry in Table 6.1 (3). These are the parameters commonly required and are to be used as a minimum guideline where exact permit specifications do not exist.

6.6.2 Other Parameters

Application of the techniques from Section 4.4 is a rational method of establishing parameters to measure. However, if process control is desired, measure the critical constituent. For example, if a distillation tower is to be controlled, monitoring the organic carbon content of the discharge stream may provide early information of leaks in the system.

6.7 TYPE OF SAMPLE

In any program, the type of sample, either composite or grab, must be established. Permit restrictions will determine the type for effluent monitoring but for in-plant surveys, both types should be considered and the most appropriate chosen.

Collect grab samples in the following situations:

1. If a batch discharge is to be characterized.
2. If the flow is homogeneous and continuous with relatively constant waste characteristics so a grab sample is representative of the stream.
3. When the extremes of flow and quality characteristics are needed (e.g., for design purposes).
4. When one is sampling for a parameter which requires that the entire sample be used for analysis with no interior transfers of containers (e.g., oil and grease).
5. When sampling for parameters which change character rapidly such as dissolved gases or those which cannot be held for a long length of time before analysis (e.g., bacteria counts, chlorine, dissolved oxygen and sulfide).

Table 6.1. NPDES EFFLUENT LIMITATION PARAMETERS BY INDUSTRY

	Dairy Products	Grain Mills	Canned & Preserved Fruit & Veg.	Canned & Preserved Seafood	Sugar Products	Textiles	Cement	Feedlots	Electroplating	Organic Chemicals	Inorganic Chemicals	Plastics & Synthetics	Soap & Detergents	Fertilizer Mfg.	Petroleum Refining	Iron & Steel Mfg.	Non-Ferrous Metals	Phosphate Mfg.	Stationary Electric Power Generating Equip	Ferroalloy Mfg.	Leather Tanning and Finishing	Glass Manufacturing	Asbestos Mfg.	Rubber Products	Timber Products	Pulp, Paper, etc.	Builders Paper & and Board	Meat Products	Printure Ink and Paint	Paving & Roofing Materials
Temperature Discharges					X		X												X											
BOD - 5 Day	X	X	X	X	X	X		X		X		X	X		X				X		X	X		X	X	X	X	X	X	X
Suspended Solids	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X
Oils, Fats & Grease				X		X							X		X	X			X		X	X		X				X		X
Ammonia														X	X	X	X		X									X		
Nitrite-Nitrogen																			X											
Nitrate-Nitrogen														X		X			X											
Nitrogen (Kjeldahl)														X					X											
Phosphorus														X				X			X	X								
Sulfite																			X											
Sulfide						X									X	X			X		X									
Sulfate																														
Chloride																														
Chlorine																														
Fecal Coliform Bact.					X	X		X																						
Fluoride											X			X		X	X	X			X							X		
Arsenic																														
Barium																														
Boron																														
Cadmium																														
Chromium						X			X		X	X			X				X	X	X									
Cobalt																														
Copper									X								X													

Table 6.1 (Continued). NPDES EFFLUENT LIMITATION PARAMETERS BY INDUSTRY

	Dairy Products	Grain Mills	Canned & Preserved Fruit & Veg.	Canned & Preserved Seafood	Sugar Products	Textiles	Cement	Feedlots	Electroplating	Organic Chemicals	Inorganic Chemicals	Plastics & Synthetics	Soap & Detergents	Fertilizer Mfg.	Petroleum Refining	Iron & Steel Mfg.	Non-Ferrous Metals	Phosphate Mfg.	Stationary Electric Power Generating Equip	Ferroalloy Mfg.	Leather Tanning and Finishing	Glass Manufacturing	Asbestos Mfg.	Rubber Products	Timber Products	Pulp, Paper, etc.	Builders Paper & Board	Meat Products	Printing Ink and Paint	Paving & Roofing Materials
Lead											X					X			X											
pH	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Manganese																X			X	X										
Mercury											X								X											
Nickel									X										X											
Zinc									X			X				X			X											
Phenols						X				X		X				X			X											
PCB_5																														
Aldrin																														
Dieldrin																														
Heptachlor																										X				
Color						X																								
COD						X				X	X	X	X		X		X					X	X	X	X					
Cyanide									X	X						X			X	X										
Iron										X																				
Surfactants													X																	
Aluminum																		X												
Arsenic																		X									X			
Settleable Solids																														

Collect or form composite samples in the following situations:

1. If the average characteristics of a flow stream are to be established over a certain period of time.

2. If performing individual analyses on all the discrete portions of a composite does not give sufficient information or merit the extra cost.

3. When the parameters to be measured are not adversely affected by the time lag between sampling and analyses.

If composite samples are to be taken, the specific type of composite must be established. This is contingent upon economic factors and the type of discharge (batch or continuous) to the sampling point. The restrictions on common types of composites are listed in Table 6.2.

Table 6.2 TYPES OF COMPOSITES FOR DIFFERENT DISCHARGES

Sample Type	Mostly Continuous Discharges	Batch (and Continuous) Discharges	Cost
1. Continuous-volume proportional to flow rate	Best	Best	Highest
2. Periodic-time proportional to flow since last sample	Better	Adequate	Medium
3. Periodic-time constant volume constant plus manual composite	Adequate	Adequate only with grab samples of batch discharges	Lowest

6.8 METHOD OF SAMPLING

Choose manual or automatic sampling depending on how the advantages and disadvantages of the methods apply to the specific sampling program (Tables 6.3 and 6.4).

Table 6.3. THE ADVANTAGES AND DISADVANTAGES OF MANUAL AND AUTOMATIC SAMPLING

Type	Advantages	Disadvantages
Manual	Low capital cost	Probability of increased variability due to sample handling
	Compensate for various situations	Inconsistency in collection
	Note unusual conditions	High cost of labor
	No maintenance	Repetitious and monotonous for personnel
	Can collect extra samples in short time when necessary	
Automatic	Consistent samples	Considerable maintenance for batteries & cleaning; susceptible to plugging by solids
	Probability of decreased variability caused by sample handling	Restricted in size to the general specifications
	Minimal labor requirement for sampling	Inflexibility
	Has capability to collect multiple bottle samples for visual estimate of variability & analysis of individual bottles	

Table 6.4. COMPARISON OF REQUIREMENTS AND FEATURES OF AUTOMATIC AND MANUAL METHODS

Sampling Constituents	Method of Choice	
	Automatic	Manual
Length of Program:		
Long	X	
Short		X
Manpower Available:		
24 hour operation (i.e. shift worker available)		X
Special provision needed for work over 8 hours	X	
Availability of Automatic Sampler Which Meets Program Needs:		
Yes	X	
No		X
Accessibility to Sampling Point:		
Good		X
Poor	X	
Number of Sampling Points:		
Many		X

6.9 AUTOMATIC SAMPLERS

If an automatic sampler is to be used, the actual type of sampler is determined by the constituents in the wastewater. A list of samplers is indicated in Section 2.3.1 and the features and techniques for use of automatic samplers are discussed in Section 2.3.2. To choose a sampler, list the features needed for sampling the type of industrial wastewater. If the variability of the wastewater is not known or expected to be high, a multiplex feature which takes more than one sample into a single bottle is desirable. This would allow samples to be collected at short time increments such as once every 10-15 minutes. Another possible feature would be to fill more than one sample bottle at a time interval.

This multiple bottle technique would allow use of one bottle for the composite and the other for possible discrete analysis. Once the needed features have been established, the sampler which best matches these features can be selected. Available samplers may need adaptation. It is imperative that the stream be well mixed at the sampling point to avoid problems when using automatic samplers in streams with a high solids content.

6.10 VOLUME OF SAMPLE AND CONTAINER TYPE

The volume of sample to be taken is determined by the number of analyses to be performed on the sample. If this has not been determined, a grab sample volume of 3.8 l (1 gal.) and an individual composite volume of 0.4 l (0.11 gal.) should be taken. The container type is also contingent upon the analysis to be run. If there is any possibility of high organic content in the sample, borosilicate glass must be used; otherwise conventional polyethylene is acceptable.

6.11 PRESERVATION AND HANDLING OF SAMPLES

This procedure is contingent upon the types of parameters to be analyzed. Specific techniques are indicated by the parameter in Chapter 10.

6.12 FLOW MEASUREMENT

6.12.1 Open Channel Flow

Open channel flow devices have been discussed in detail in Section 2.4.3 and should be used for effluent monitoring or determining the addition of flow between two sewers.

6.12.2 Other Flow Measurement

Various methods of closed pipe or free discharge flow measurement may be applicable for in-plant surveys. In-depth discussions of these devices are available in the literature (4,5,6,7). These devices include:

1. Flow nozzle
2. Orifice meter
3. Pitot tube
4. Magnetic meter
5. Venturi meter
6. Elbow meter

More information on these devices is included in Section 2.4.

6.13 REFERENCES

1. Federal Water Pollution Control Act, as amended 33 USC 1251 et seq. 86 Stat. 816, Public Law 92-500.

2. Black, H. H. Procedure for Sampling and Measuring Industrial Waters. Sewage Ind. Wastes. 24:45, January 1952.

3. N.F.I. C-Denver. Effluent Limitations Guidelines for Existing Sources and Standards of Performance for New Sources for 28 Point Source Categories. Denver, p. 122, August 1974.

4. EPA Technology Transfer. Handbook for Monitoring Industrial Wastewater, August 1973.

5. Bouveng, H. O. Guide to Flow Measurement and Sampling with Special Reference to Pulp and Paper Mill Wastewater Systems. Pur and Appl. Chemistry. 19:267-290, 1969.

6. Chow, V. T. Handbook of Applied Hydrology. New York, McGraw-Hill, 1964.

7. Water Measurment Manual, Second Edition. Bureau of Reclamation, U.S. Department of the Interior, Washington, D.C., 1967.

CHAPTER 7

SAMPLING SURFACE WATERS AND BOTTOM SEDIMENTS

7.1 BACKGROUND

The sampling of rivers and streams, estuaries, lakes and oceans and their associated bottom sediments are considered in this chapter. Methods of sampling are directly affected by the objectives of the study and parameters which are to be analyzed. Therefore, the decisions regarding parameters must be made at the beginning of the study in order to develop a rational sampling program.

7.2 OBJECTIVES OF THE STUDY

The main objectives of sampling surface waters and sediments are:

1. Evaluation of the standing crop, community structure, diversity, productivity and stability of indigenous aquatic organisms.
2. Evaluation of the quality and trophic state of a water system.
3. Determination of the effect of a specific discharge on a certain water body.

7.3 PARAMETERS TO ANALYZE

Selection of parameters is dependent on the objectives and extent of the program or study and must be performed prior to the development of the sampling plan. Surface waters and sediments are commonly analyzed for the chemical and biological parameters listed in Table 7.1.

Table 7.1. COMMON ANALYSES FOR SURFACE WATER AND SEDIMENT SAMPLING

Chemical	Biological
Dissolved Oxygen	Fish
Phosphate	Benthic Macroinvertebrates
Nitrogen Series	Periphyton
Alkalinity	Phytoplankton
Silica	Zooplankton
pH	Macrophytes
Specific Conductance	Macroalgae
Solids (TDS, TS, TSS)	
Organic Matter and Demand	
Color	
Turbidity	
Pesticides	
Heavy Metals	

7.4 LOCATION OF SAMPLING POINTS

Select the study site based on the program objectives, the parameters of interest, and the sampling units. For example, the following guidelines are suggested in the EPA Model State Water Monitoring Program (1) for selecting long-term biological trend monitoring stations:

1. At key locations in water bodies which are of critical value for sensitive uses such as domestic water supply, recreation, propagation, and maintenance of fish and wildlife.

2. In major impoundments near the mouths of major tributaries.

3. Near the mouths of major rivers where they enter an estuary.

4. At locations in major water bodies potentially subject to inputs of contaminants from areas of concentrated urban, industrial, or agricultural use.

5. At key locations in water bodies largely unaffected by man's activities.

In order to avoid bias, use one of the following random sampling plans to determine sampling points within the study site. Random sample selection is discussed in more detail in the EPA Biological Field and Laboratory Methods Manual (2).

7.4.1 Simple Random Sampling

Use a simple random sampling plan when there is no reason to subdivide the population from which the sample is drawn. Then the sample is drawn such that every unit of the population has an equal chance of being selected. First, number the universe or entire set of sampling units from which the sample will be selected. This number is N. Then from a table of random numbers select as many random numbers, n, as there will be sampling units selected for the sample. Select a starting point in the table and read the numbers consecutively in any direction (across, diagonal, down, up). The number of observations, n (sample size), must be determined prior to sampling. For example, if n is a two-digit number, select two-digit numbers ignoring any number greater than n or any number that has already been selected. These numbers will be the numbers of the sampling units to be selected.

7.4.2 Stratified Random Sampling

Use a stratified random sampling plan if any knowledge of the expected size or variation of the observations is available. To maximize precision, construct the strata such that the observations are most alike within strata and most different among strata, i.e., minimum variance within strata and maximum variance among strata. Perhaps the most profitable means of obtaining information for stratification is though a prestudy reconnaissance (a pilot study). For information on conducting a pilot study, consult the EPA Biological Methods Manual (2). Stratification is often based upon depth, bottom type, isotherms, or other variables suspected of being correlated with the parameter of interest. Select as many strata as can be handled in the study. In practice, however, gains in efficiency due to stratification usually become negligible after only a few divisions unless the characteristic used as the basis of stratification is very highly correlated with the parameter of interest (2).

7.4.3 Systematic Random Sampling

Use a systematic random sampling plan to assure an adequate cross section while maintaining relative ease of sampling. A common method of systematic sampling involves the use of a transect or grid. However, choose a random starting point along the transect or grid to introduce the randomness needed to guarantee freedom from bias and allow statistical inference.

7.4.4 Nonrandom Sampling

Use a nonrandom sampling plan if justified by the study site, or parameters of interest, or the type of study being undertaken. For example, the following sample locations might satisfy the program objectives:

Parameter	Sampling Location
Fish	Shoreline sampling
Benthic macroinvertebrates	Right, left bank, midstream or transect
Periphyton	Shoreline sampling
Phytoplankton	Transect or grid
Zooplankton	Transect or grid
Macrophytes	Shoreline sampling or transect
Chemical	Transect or grid

7.4.4.1 Impact of Point Discharges - A transect sampling scheme may be used to determine the impact of a point discharge.

1. Place lines transecting the receiving water at various angles from the discharge point.

2. Choose sampling intervals randomly or uniformly or by the methods described in Section 7.4.4.2.

3. Choose two remote control points to use as background.

4. See Figure 7.1 for example.

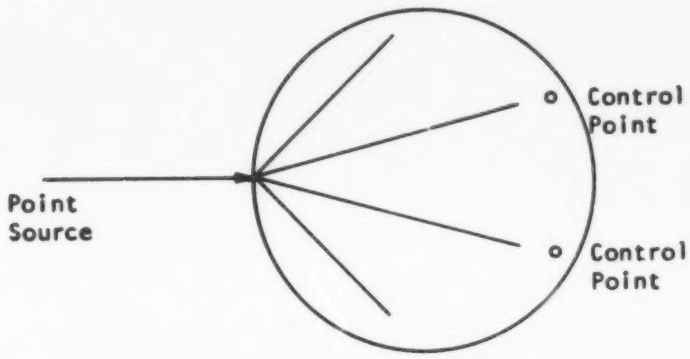


Figure 7.1. Example of transect sampling scheme

A grid sampling scheme may also be used but is not applicable to all biological parameters. Grid placement must be contained in a similar environment (e.g. all ripples or all pools) for a valid comparison.

1. Set up grids across and through the area to be sampled (i.e., in both width and depth directions versus length) as required by the program.

2. The grid size is dependent upon the degree of lateral and vertical mixing. If the amount of mixing is unknown, then take a larger number of samples across and through the stream than would be otherwise desirable.

3. Choose the number of samples randomly, uniformly or using the procedure in Section 7.4.4.2.

4. Choose a control point upstream of the grit system.

5. See Figure 7.2 for an illustration of the grid method.

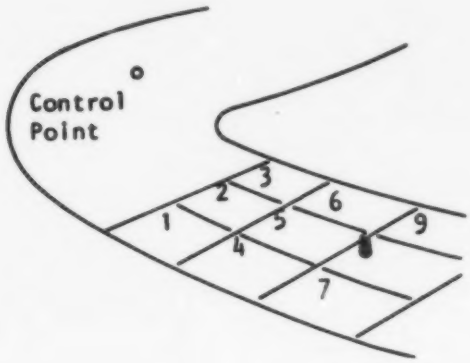


Figure 7.2. Example of grid sampling scheme

7.4.4.2 Spatial Gradient Technique - This technique may be used for the rational selection of sampling station locations (3,4). It presupposes the existence of historical data or some reasonable estimate of the expected variability of the parameters to be monitored over the region of interest, say, along the length of the river. This technique has greater applicability for chemical than biological parameters.

1. Collect historical or comparable data to estimate the mean and variance of the parameter of interest, Y.

2. Plot the maximum and minimum values of the parameter concentration versus distance along the river (Figure 7.3).

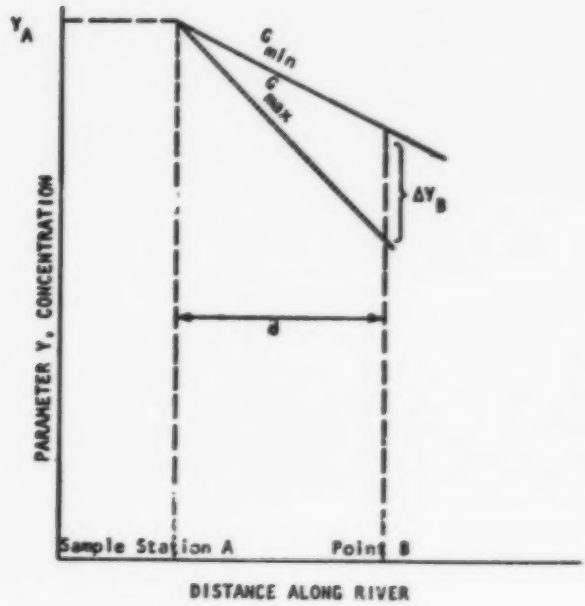


Figure 7.3. Use of spatial gradient technique for maximum spacing of sampling stations

3. Calculate a slope for both lines (G_{max} and G_{min}).

4. Determine the difference between the slopes, i.e., $G_{max} - G_{min}$

5. Determine the maximum allowable error in the estimates of the parameter value at Point B.

6. $$d_{max} = \frac{\Delta Y_{max}}{G_{max} - G_{min}}$$

7. Use this d to determine distance between points on a transect or grid in a grid pattern.

7.5 NUMBER OF SAMPLES

The following information is summarized from the EPA Biological Methods Manual (2).

7.5.1 Simple Random Sampling

Use one of the following two methods depending on the decision variable.

1. Estimation of a Binomial Proportion - An estimate of the proportion of occurrence of the two categories must be available. If the categories are presence and absence, let the probability of observing a presence of P ($0 < P < 1$) and the probability of observing an absence by Q ($0 < Q < 1$, $P + Q = 1$). The second type of information which is needed is an acceptable magnitude of error, d, in estimating P (and hence Q). With this information, together with the size, n, of the population, the formula for n as an initial approximation (n_o), is:

$$n_o = \frac{t^2PQ}{d^2}$$

   a. For $n_o > 30$, use $t = 2$. This n_o ensures with a 0.95 probability that P is within d of its true value.

   b. For $n_o < 30$ use a second calculation where t is obtained from a table of "Student's t" with $n_o - 1$ degrees of freedom. If the calculation results in an n_o, where

$$\frac{n_o}{N} < 0.05$$

   no further calculation is warranted. Use n_o as the sample size. If $\frac{n_o}{N} > 0.05$, make the following computation:

$$n = \frac{n_o}{1 + \frac{n_o - 1}{N}}$$

2. Estimation of a Population Mean for Measurement Data - In this case an estimate of the variance, S^2, must be obtained from some source, and a statement of the margin of error, d, must be expressed in the same units as are the sample observations.

   a. For $n_o > 30$, use: $n_o = \frac{t^2s^2}{d^2}$

   b. For $n_o < 30$, recalculate using t from the tables, and if $\frac{n_o}{N} > 0.05$, a further calculation is in order:

$$n = \frac{n_o}{1 + \frac{n_o}{N}}$$

After a sample of size, n, is obtained from the population, the basic sample statistics may be calculated. If the sample size, n, is greater than 5 percent of the population ($\frac{n}{N} > 0.05$), a correction factor is used so that the calculation for the sample variance is:

$$s^2 = \frac{N-n}{N} \cdot \frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n-1}$$

7.5.2 Stratified Random Sampling

Conduct a pilot study or obtain from other sources reliable estimates of the variance within strata. If historical data has been collected, use optimal allocation to determine the total number of samples.

$$n = \frac{\frac{t^2(\Sigma N_k s_k)^2}{N^2 d^2}}{1 + \frac{t^2 \Sigma N_k s_k^2}{N^2 d^2}}$$

where t = Student's t value (use 2 for estimate)

N_k = number of sampling units in stratum k

s_k^2 = variance of stratum k

$s_k = \sqrt{s_k^2}$ = standard deviation of stratum k

N = total number of sampling units in all strata

d = acceptable parameter error

If no data is available, use proportional allocation to determine the total number of samples:

$$n = \frac{\frac{t^2 \Sigma N_k s_k^2}{Nd^2}}{1 + \frac{\Sigma N_k s_k^2}{N^2 d^2}}$$

Use the following equations to determine the number of samples to be collected in each stratum, n_k:

Optimal allocation: $n_k = \frac{nN_k s_k}{\Sigma N_k s_k}$

Proportional allocation: $n_k = \frac{nN_k}{N}$

7.5.3 Systematic Random Sampling

Determine the number of samples to be taken on the grid or transect using the methods given in Section 7.4.4.2 or 7.5.1.

7.6 FREQUENCY OF SAMPLING

While the frequency of sampling will often be determined by the program, use the Model State Water Monitoring Program (1) guidelines for guidance in trend monitoring (Table 7.2).

7.7 METHOD OF SAMPLING

While compositing of individual grab samples is permitted for most chemical parameters, as a rule do not composite biological samples. For biological parameters collect single grab samples in replicate. An exception would be if a single grab sample does not contain a sufficient number of the organisms to be counted or examined; then two or more grab samples may be composited.

7.8 TYPES OF SAMPLERS

Choose the type of sampler that meets the needs of the sampling program by considering the advantages and disadvantages of the sampler type. In general, equipment of simple construction is preferred due to ease of operation and maintenance plus lower expense. Advantages and disadvantages of various water bottles are shown in Table 7.3 and illustrated in Figure 7.4. This equipment is useful for chemical, phytoplankton and zooplankton sampling. Corers and bottom grabs (Tables 7.4 and 7.5 and Figures 7.5 and 7.6) are useful for sediment sampling. Nets and substrate samplers are covered in Tables 7.6 and 7.7 and Figures 7.7 and 7.8. There are inherent advantages of using a diver for sediment sampling. The diver can ascertain what is a representative sample in addition to taking pictures and determining qualitatively the current velocity.

Table 7.2. MODEL STATE WATER MONITORING PROGRAM GUIDELINES FOR BIOLOGICAL MONITORING (1)

Community	Parameter	Priority[a]	Collection & analysis method[b]	Sampling frequency[c]
Plankton	Counts and identification; Chlorophyll a; Biomass as ash-free weight	1	Grab samples	Once each; in spring, summer and fall
Periphyton	Counts and identification; Chlorophyll a; Biomass as ash-free weight	1 2 2	Artificial substrates	Minimally once annually during periods of peak periphyton population density and/or diversity.
Macrophyton	Areal coverage; Identification; Biomass as ash-free weight	2 2 2	As circumstances prescribe	Minimally once annually during periods of peak macrophyton population density and/or diversity
Macroinvertebrate	Counts and identification Biomass as ash-free weight Flesh tainting; Toxic substances in tissue[d]	1 2 2 2	Artificial and natural substrates	Once annually during periods of peak macroinvertebrate population density and/or diversity
Fish	Toxic substances in tissue[d] Counts and identification; Biomass as wet weight; Condition factor; Flesh tainting Age and growth	1 2 2 2 2	Electrofishing or netting	Once annually during spawning runs or other times of peak fish population density and/or diversity

a Priority: 1) Minimum program; 2) Add as soon as capability can be developed.
b See EPA Biological Methods Manual. c. Keyed to dynamics of community.
d See Analysis of Pesticide Residues in Human and Environmental Samples, "USEPA, Perrine Primate Research Lab, Perrine, FL 32157 (1970)," & "Pesticide Analytical Manual," USDHEW, FHA, Wash, D.C.

Table 7.3. COMPARISON OF WATER SAMPLERS

Device	Application	Container Type	Advantages	Disadvantages
Nansen Bottle	Phytoplankton	Teflon lined	Able to use in series for deep water	Small volume
Simple Bottle	Chemical Bacteriological	Glass	Easy to make	Cross contamination
Kemmerer Bottle	Chemical Bacteriological Zooplankton Phytoplankton	PVC Brass Acrylic plastic Nickel-plated brass	No cross contamination, no problem with avoidance, point sample	Fixed capacity from 0.4-16 l.
Van Dorn Bottle	Chemical Bacteriological Zooplankton Phytoplankton	PVC	No cross contamination, point sample, no avoidance problem	Fixed capacity from 2-30 l.
Pumps	Chemical Zooplankton Phytoplankton	Vanes	Large volume, samples a vertical water column, continuous sample	Bulky, non representative

Table 7.4. COMPARISON OF BOTTOM GRABS

Device	Advantages	Disadvantages
Ponar	Safe, easy to use, prevents escape of material with end plates, reduces shock wave, combines advantages of others, preferred grab in most cases	Can become buried in soft sediments
Ekman	Use in soft sediments and calm waters, collects standard size sample (quantitative), reduces shock wave	Not useful in rough water; not useful if vegetation on bottom
Tall Ekman	Does not lose sediment over top; use in soft sediments and calm water, standard sample size, reduces shock wave	Not useful in rough waters, others as for Ekman
Peterson	Quantitative samples in fine sediments, good for hard bottoms and sturdy and simple construction	May lose sampled material, premature tripping, not easy to close; does not sample constant areas; limited sampling capacity
Smith-Mcintyre	Useful in bad weather, reduces premature tripping, use in depths up to 1500 m (3500 ft), flange on jaws reduced material loss, screen reduces shock waves, good in all sediment types	Large, complicated and heavy, hazardous, for samples to 7 cm depth only, shock wave created
Hayward Orange Peel	Easy to operate, commercially available in various sizes, does not rust easily, does not require messenger, good bottom penetration, takes undistrubed sample of top sediment	Difficult to determine sampling cover, 2 cables required, active washing during sampling, jaws do not close tightly, soft sediment fouls closing mechanism
Diver	Can determine most representative sampling point and current velocity	Requires costly equipment and special training

Table 7.5. COMPARISON OF CORING DEVICES

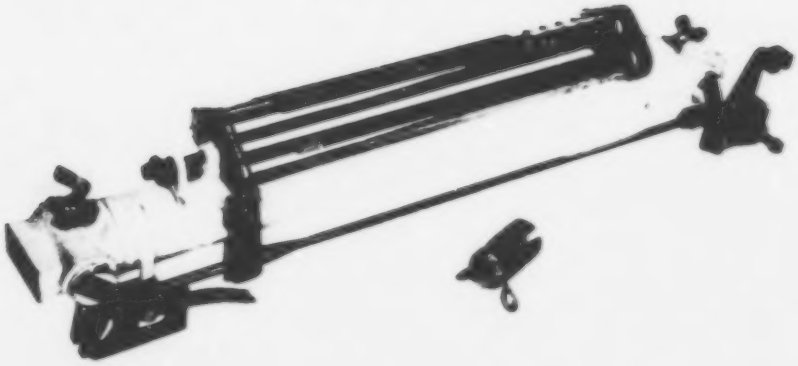
Device	Advantages	Disadvantages
Kajak or K.B. Corer	Does not impede free flow of water, no pressure wave, easily applied to large area	
Moore (Pfleger)	Valve allows sample to be held	Careful handling necessary to avoid sediment rejection, not in soft sediments
O'Connor	Can sample water with hard bottoms	Not in deep water
Elgmork's	Sample easily removed, good in soft muds, easy to collect, easy to remove sample	Not in hard sediments
Jenkins	Good in soft sediments and for collecting an undisturbed sediment-water interface sample. Visual examination of benthic algal growth and rough estimates of mixing near the interface after storms can be made	Complicated
Enequist	Good in soft/medium sediments, closing mechanism	Does not penetrate hard bottom
Kirpicenko	Soft and hard bottoms, various sizes, closes automatically	Not for stony bottoms

Table 7.6. COMPARISON OF NET SAMPLING DEVICES

Devices	Application	Advantages	Disadvantages
Wisconsin Net	Zooplankton Phytoplankton	Efficient shape concentrates sample	
Closing Net	Zooplankton	Samples one stratum	Qualitative
Clarke-Bumpus	Zooplankton	Quantitative	No point sampling, difficult to get correct speed, clean bottom only
Juday Plankton Trap	Zooplankton	No cross contamination between samples, minimal avoidance, large volume	Bulky and heavy, calm water only, clean bottom only, primarily research tool

Table 7.7. COMPARISON OF SUBSTRATE SAMPLERS

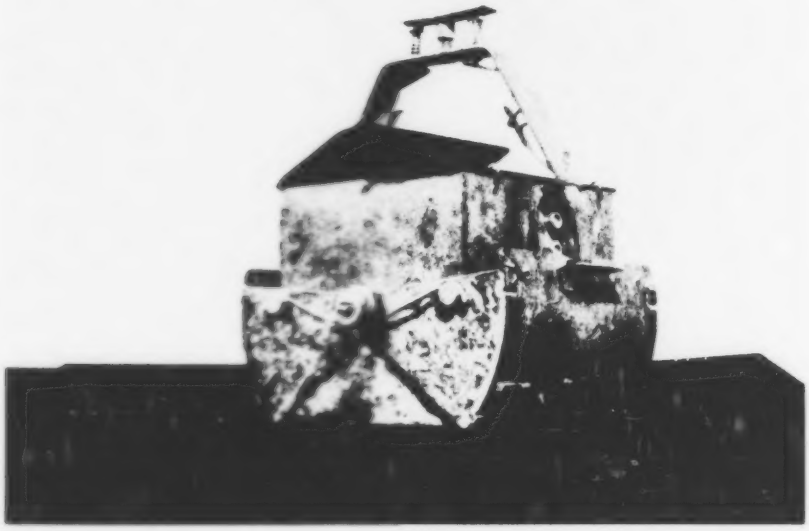
Type of Substrate	Advantages	Disadvantages
1. Artificial		
Hester-Dendy	Reduces compounding effects of substrate differences, multiplate sampler	Long exposure time, difficult to anchor, easily vandalized
Fullner	Higher precision than Hester-Dendy, wider variety of organisms	Same as Hester-Dendy
EPA Basket Type	Comparable data, limited extra material for quick lab processing	No measure of pollution on strata, only community formed in sampling period
EPA Periphyton Sampler	Floats on surface, easily anchored, glass slides exposed just below surface	May be damaged by craft; easily vandalized
2. Natural		
Any bottom or sunken material	Indicate effects of pollution, gives indication of long term pollution	Possible lack of growth



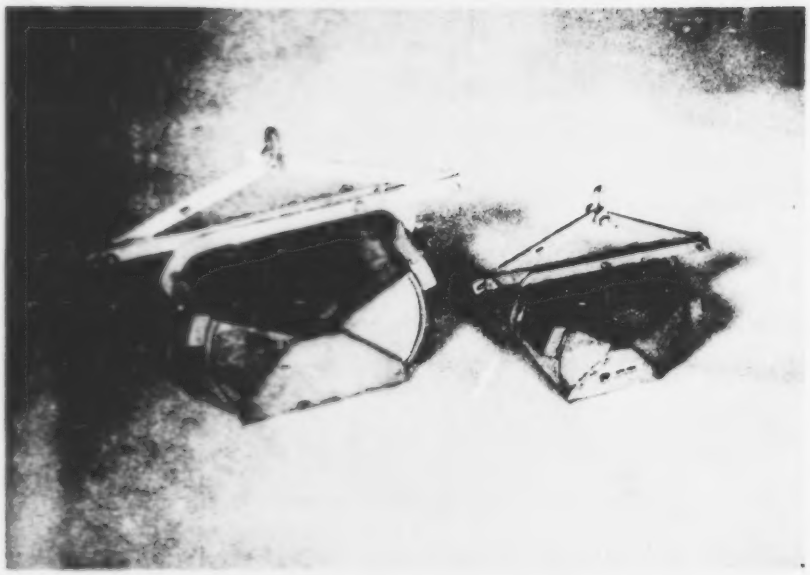
Nansen Water Bottle

Brass Kemmerer Water Bottle

Figure 7.4 Water bottles
(Courtesy of Wildlife Supply Co.)

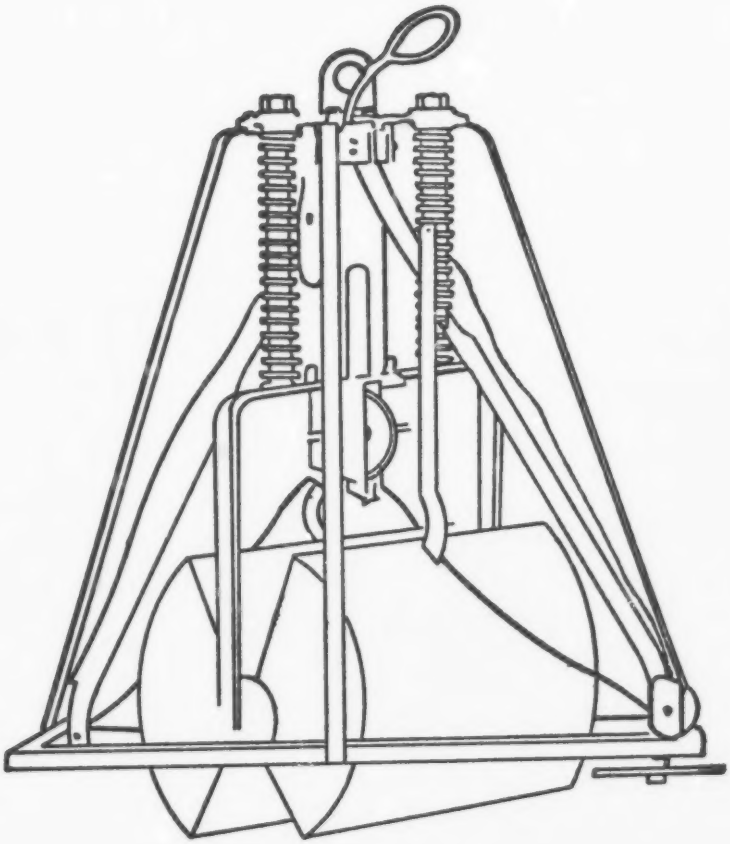


Ekman Grab



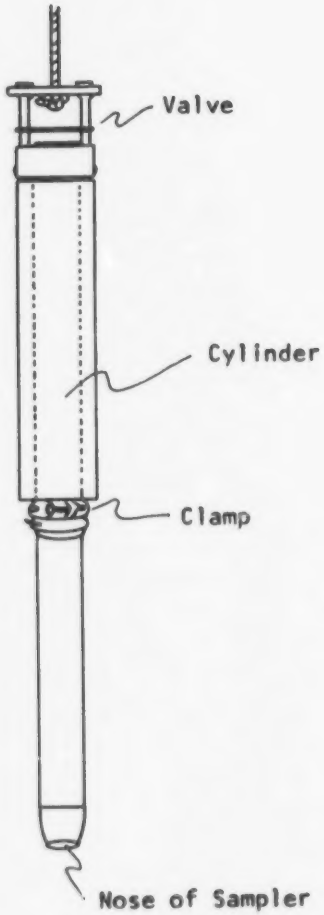
Bonar Sampler (two sizes)

Figure 7.5. Bottom grab samplers
(Courtesy of Wildlife Supply Co.)

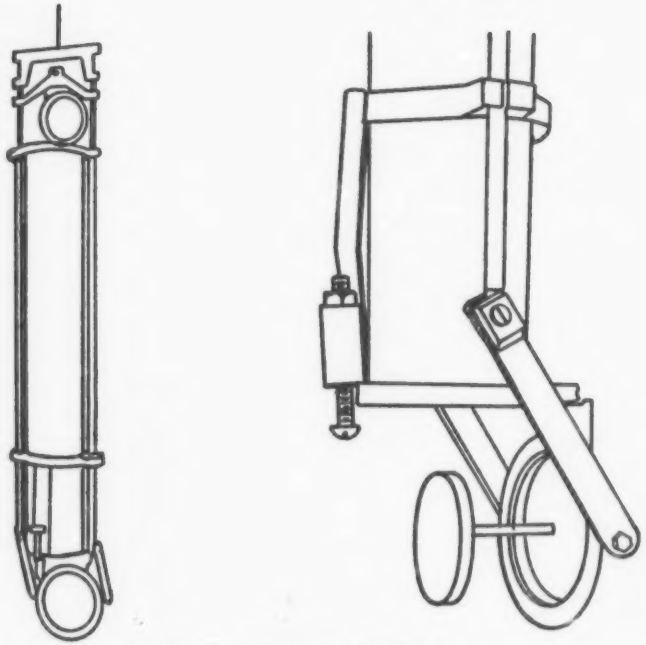


Smith-McIntyre (Aberdeen) Grab

Figure 7.5 (continued). Bottom grabs



Side View-Vertical Core Sampler



Elgmork's Core Sampler

Figure 7.6. Core samplers

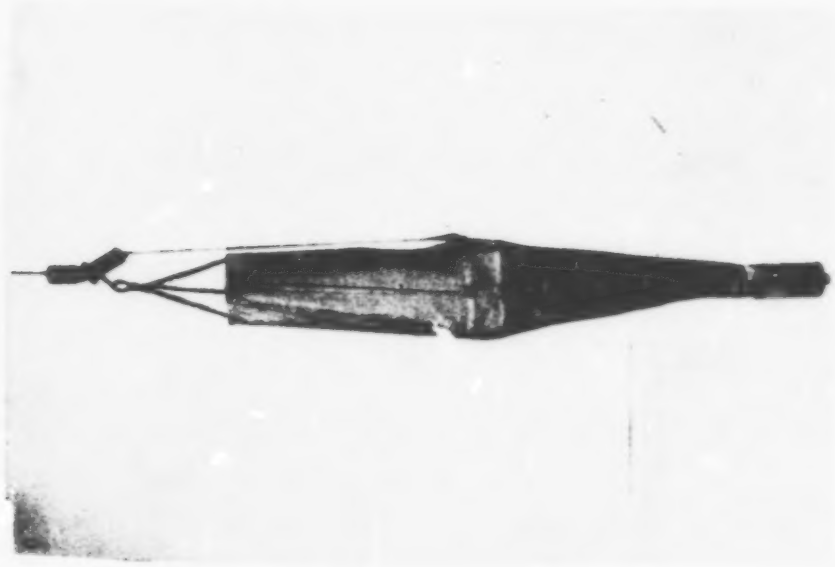
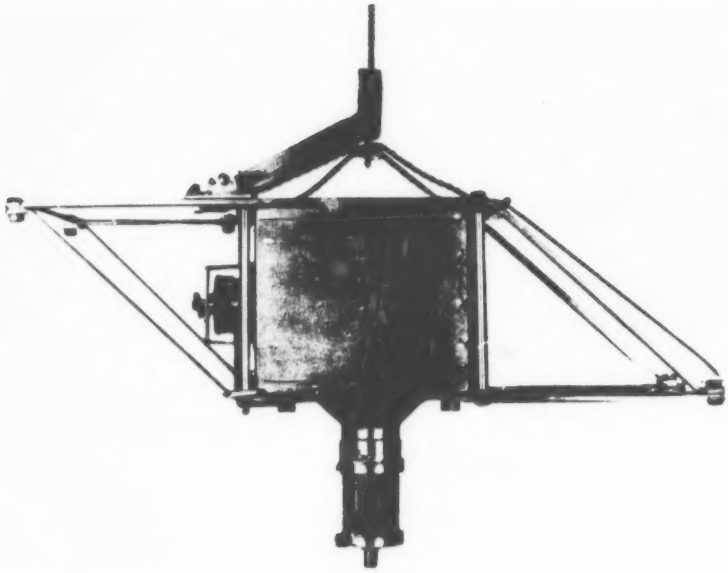
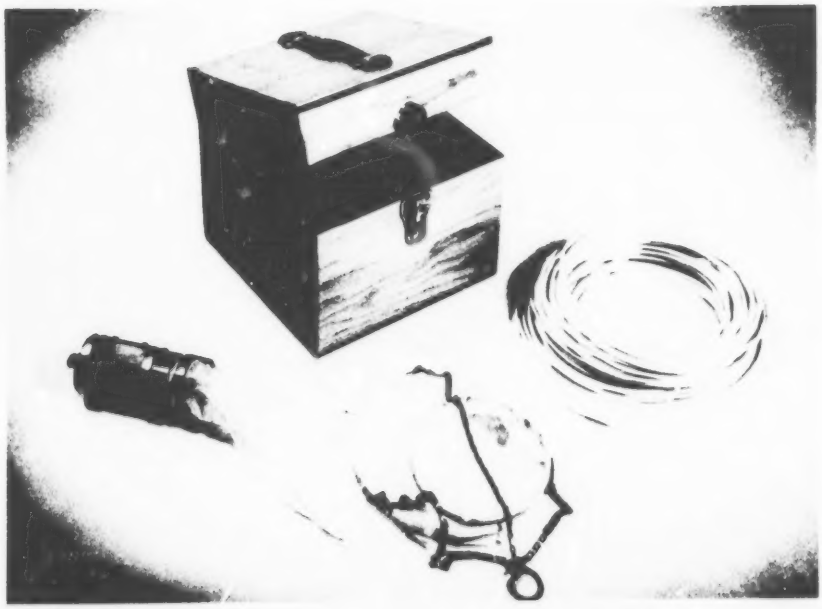


Figure 7.7. Nets and related samplers
(Courtesy of Wildlife Supply Co.)

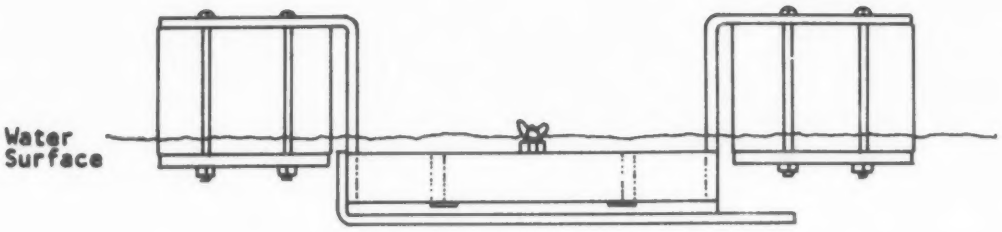


Juday Plankton Trap

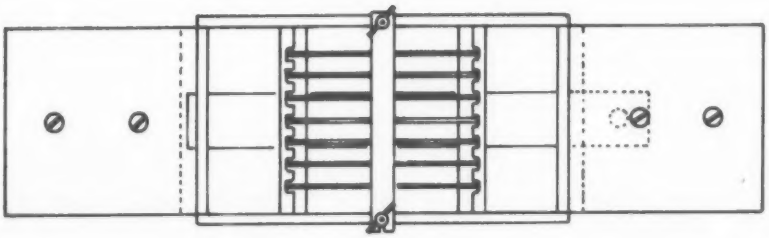


Wisconsin Net

Figure 7.7 (continued). Nets and related samplers
(Courtesy of Wildlife Supply Co.)



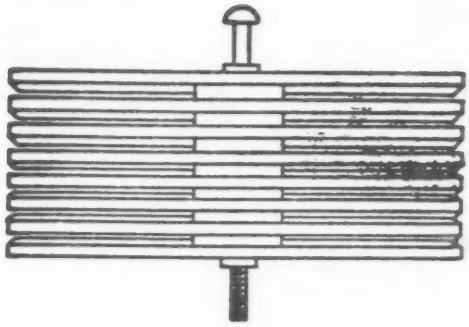
Side View



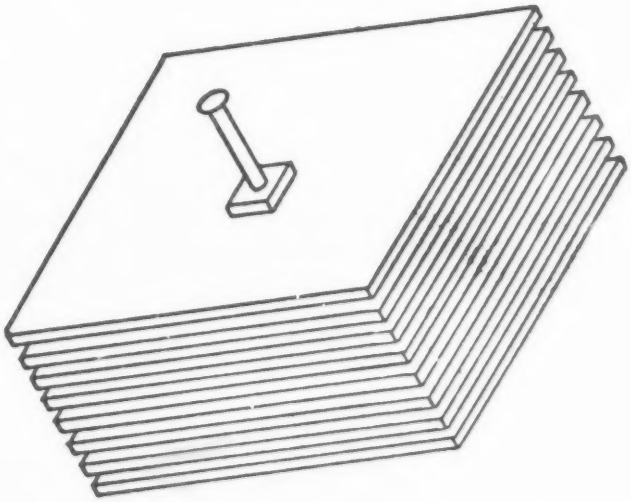
Top View

EPA Periphyton sampler. Plexiglass frame supported by two styrofoam floats. Rack holds eight glass microscope slides (30).

Figure 7.8. Periphyton samplers.



Side View



Hester-Dendy

Figure 7.9. Macroinvertebrate sampler

7.9 VOLUME OF SAMPLE AND CONTAINER TYPE

The size of sample is dependent on the expected amount of the parameter to be analyzed. The container type is also dependent on parameter type. Refer to Section 10.7 for specific information relative to the parameters which are to be analyzed.

7.10 PRESERVATION AND HANDLING OF SAMPLES

Refer to Section 10.7 for specific information regarding preservation and handling of samples relative to the parameters to be analyzed. There is little or no published information on the preservation of bottom sediment samples. Therefore, no specific techniques can be recommended at this time.

7.11 FLOW MEASUREMENT

Flow measurement in rivers is accomplished by the combined use of a current meter to measure the stream velocity and a stage recorder to measure the surface elevation of the river. Consult USGS gaging stations for additional or historic information. See Section 2.4 for more details.

7.12 REFERENCES

1. National Water Monitoring Panel. Model State Water Monitoring Program. U.S. EPA. Report No. EPA-440/9/74-002. U.S. EPA Office of Water and Hazardous Materials. June 1975.

2. Weber, C. I., ed. 1973. Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents. National Environmental Research Center, Office of Research and Development, U.S. EPA, Cincinnati, Ohio.

3. Hill, R. F. Planning and Design of a Narragansett Bay Synoptic Water Quality Monitoring System. NEREUS Corp., 1970.

4. Drobny, N. L. Monitoring for Effective Environmental Management. Proc. ASCE National Water Resources Engineering Meeting. Atlanta, Georgia. January 24-28, 1972.

CHAPTER 8

SAMPLING AGRICULTURAL DISCHARGES

8.1 BACKGROUND

Agricultural discharges can be separated into two broad wastewater categories: 1. concentrated animal waste or manure from a confined feedlot; 2. runoff from an agricultural watershed. These two types of wastewater differ mainly in the concentration of pollutants. Runoff from fields, associated almost entirely with rainfall and snowmelt events, is characteristically much less polluted, while feedlot runoff is a highly concentrated point source. The values for constituents of field runoff depend on the amount and intensity of rainfall or snowmelt, land use, topography, soil type, use of manure or fertilizer, etc.

8.2 OBJECTIVES

There are two main objectives in sampling agricultural discharges:

1. Research - to study both field and feedlot runoff.
2. Regulatory - to monitor field or feedlot runoff or effluent from feedlot runoff treatment.

8.3 FREQUENCY OF SAMPLING

8.3.1 Feedlot Discharge

8.3.1.1 Regulatory - Follow the sampling frequency given in the discharge permit. Daily sampling is the maximum requirement in most permits.

8.3.1.2 Other - Apply the spectral analysis techniques as outlined in Section 4.4. Collect preliminary data if not available by conducting one of the following (in order of preference)

a. A one week survey collecting hourly grab samples where the discharge is continuous.

b. A 24-hour survey collecting hourly grab samples.

Calculate the mean and variances as indicated in Section 4.1 and apply a computer program for spectral analysis (Section 4.3).

8.3.2 Field Runoff

Apply the statistical methods outlined in Section 4.3 if possible. Collect preliminary data by sampling every 5 minutes for the duration of several runoff events (1). Collect and analyze samples individually or composite them proportional to flow, depending on the objectives of the study. Since most of the variability in the runoff occurs during the initial part of the runoff hydrograph on the rising side of flow crests, sampling is the most critical at this time.

8.4 LOCATION OF SAMPLING POINTS

8.4.1 Feedlot Discharge

Channel feedlot runoff to a central point by sloping or trenching if no treatment is provided. If treatment is provided, sample effluent from the treatment system.

8.4.2 Field Runoff

Select a site downstream of the runoff area at a point where runoff collects into a channelized flow. Use the topography of the area to locate this point. Choose a location with sufficient depth to cover the sampler intake without excavation.

8.5 NUMBER OF SAMPLES

The number of samples for both feedlot discharge and field runoff are calculated in the following manner:

1. Follow regulatory requirements

2. Apply the statistics in Section 4.2 after the mean and variance are determined through a preliminary survey (see Section 8.3).

8.6 PARAMETERS TO ANALYZE

8.6.1 Established by Regulation

Analyze all parameters required by discharge permits.

8.6.2 No Requirements

Analyze the following parameters (2, 3, 4):

1. Nutrients (total phosphate and nitrogen series)

2. Demand

3. Physical/Mineral (total and suspended solids)

4. Microbiological (fecal coliform and fecal streptococci)

Other analyses such as metals or pesticides may be necessary depending on the nature of the study.

8.7 TYPE OF SAMPLE

Do not collect a single grab sample due to the high variability of runoff. Collect a series of samples for analysis, or form a composite sample according to flow using one of three methods:

1. Constant sample volume, time between sampling periods proportional to stream flow.

2. Sample volume proportional to total stream flow since last sampling period; constant time between sampling periods.

3. Sample volume proportional to instantaneous stream flow rate; constant time between sampling periods.

Use method 1 whenever possible, since this technique will allow a large number of samples to be taken at high flows. Choose a flow volume increment that will not exceed the bottle supply. An automatic samplerand integrated flow measurement device is necessary for this type of sampling. Both methods 2 and 3 are acceptable also, but not preferred.

8.8 METHOD OF SAMPLING

Collect samples either automatically or manually; analyze the discrete samples separately or composite them proportional to flow. For sampling field runoff, use an automatic system activated by runoff through the flume. Typical sampling/flow measurement stations are shown in Figures 8.1 and 8.2. If feedlot runoff contains large particulate matter (e.g., corn cobs), manual sampling will be necessary.

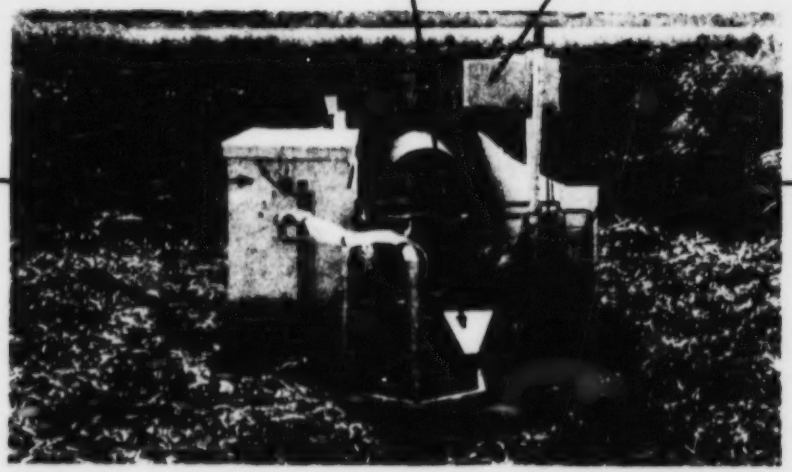


Figure 8.1 View of field installation (from 5)

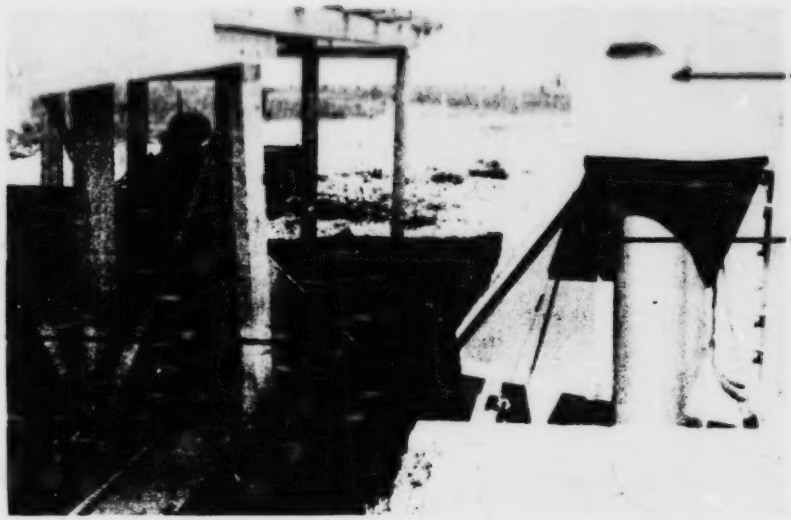


Figure 8.2. View of field installation (from 7)

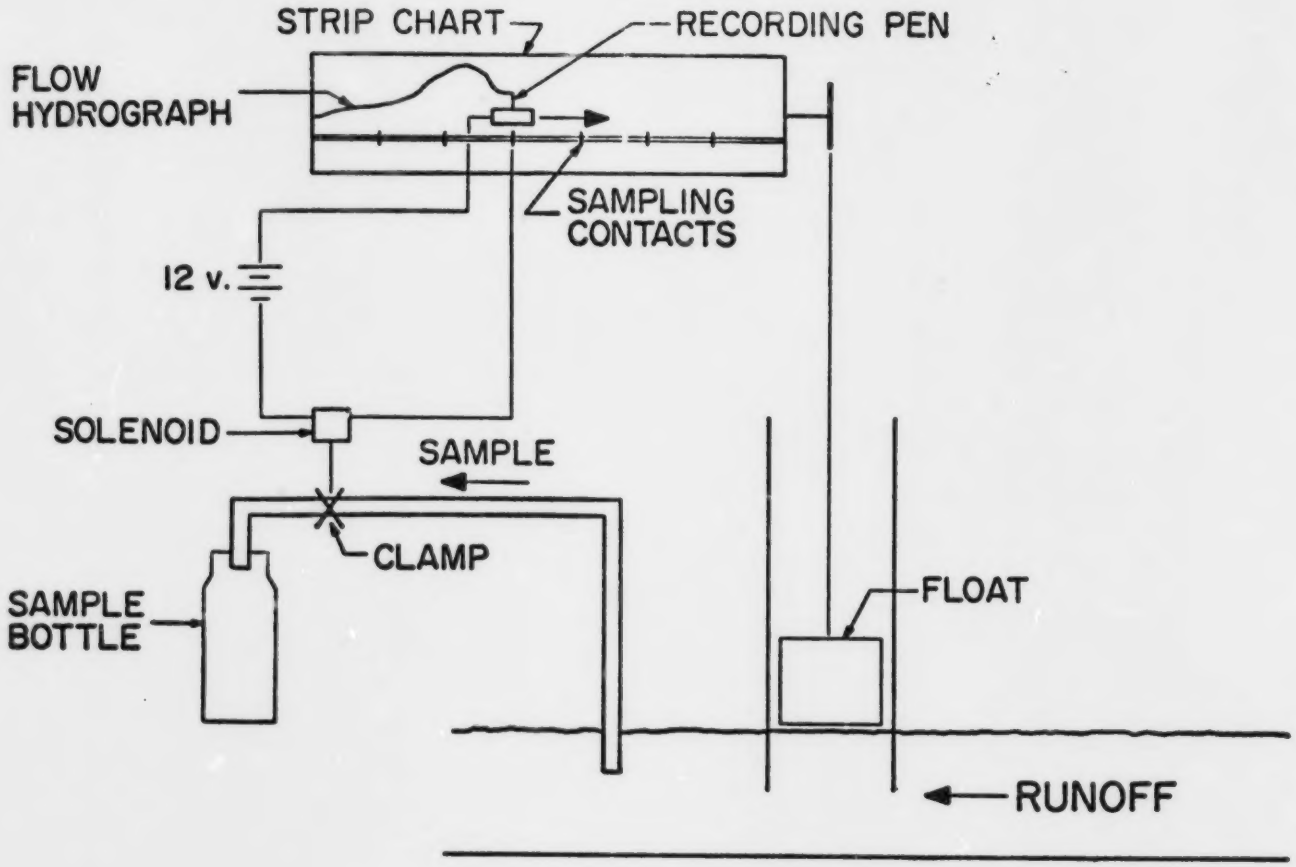


Figure 8.3. Schematic of water level recorder and sampler arrangement (from 5)

8.9 VOLUME OF SAMPLE AND CONTAINER TYPE

Use multiple sample containers to provide the best preservation for specific parameters. For example, if the parameters given in Section 8.6.2 (nutrients, demand, physical/mineral, microbiological) are to be analyzed, three containers and three preservation techniques would be required for each sample.

Container	Parameter Group	Technique
1	Nutrients	Add H_2SO_4 to pH 2 or 40-400 mg/l $HgCl_2$ and refrigerate at 4°C
2	Demand Physical/Mineral	Ice as soon as possible after collection.
3	Microbiological	Collect in sterile container and ice as soon as possible.

8.10 FLOW MEASUREMENT

Select the flow measurement device based on the specific application and the need for accuracy. A type H flume is advantageous because of its wide range of accuracy (3,6). The measurement instrumentation should include a continuously recording flow chart, with a pressure-sensitive record preferred to ink. A schematic of a typical installation is shown in Figure 8.3. More detailed information on flow measurement is given in Chapter 2.

8.11 REFERENCES

1. Miner, J.R., L.R. Bernard, L.R. Fina, G.H. Larson, and R.I. Lipper. Cattle Feedlot Runoff Nature and Behavior. Journal WPCF. 38: 834-847, October 1966.

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3. Harms, L.L., J.N. Dornbush, and J.R. Andersen. Physical and Chemical Quality of Agricultural Runoff. Journal WPCF. 46: 2460-2470, November 1974.

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CHAPTER 9

SAMPLING SLUDGES

9.1 BACKGROUND

The quantity and composition of sludge varies with the characteristics of the wastewater from which it is concentrated and with the concentration process used. Some common types of sludge are:

1. Coarse screenings from bar racks
2. Grit
3. Scum from primary settling tanks
4. Primary settling tank sludge
5. Return and waste activated sludge
6. Flotation or gravity thickened sludge
7. Aerobic or anaerobic digester sludge
8. Drying bed sludge
9. Vacuum filter cake
10. Sludge press cake
11. Centrifuge sludge
12. Fine screening backwash water
13. Sand filter backwash water
14. Sludges from special treatment processes such as the treatment of industrial wastes or combined sewer overflows.

Sludge sampling methods are usually confined to water and wastewater plants, either municipal or industrial. The sampling programs employed are concerned mainly with the following sludges: primary settling tank sludge, return and waste activated sludge, thickened sludge, digester sludge, and the resulting cakes produced by sludge drying methods.

9.2 OBJECTIVES OF SAMPLING PROGRAMS

9.2.1 Process Control

Most sludges are measured for various process control reasons including the following:

1. Optimization of sludge drawoff procedure
2. Determination of the efficiency of a concentration process
3. Determination of the loadings to the process
4. Evaluation of feed material for subsequent sludge conditioning techniques which may vary with changing feed characteristics
5. Control of the activated sludge process, i.e., the mixed liquor suspended solids (MLSS) concentration
6. Control of blanket depths in clarifiers
7. Determination of sludge characteristics that may be detrimental to digester processes

9.2.2 Research

Research projects require specific sampling techniques which are determined by the program.

9.3 PARAMETERS TO ANALYZE

The parameters to analyze will depend on the objective of the process. For example, analysis of total and suspended solids content of the sludge is necessary to determine the efficiency of a sludge thickening processes. A guide for parameters to analyze is shown in Figure 9.1. Additional parameters to analyze include: heavy metals, pesticides, and nutrients.

9.4 LOCATION OF SAMPLING POINTS

9.4.1 Flowing Sludges

9.4.1.1 Piping - Collect samples directly from the piping through a sampling cock having a minimum I.D. of 3.8 cm (1.5 in.) (1).

9.4.1.2 Channels - Collect samples at the measuring weirs, or at another point where the sludge is well mixed.

9.4.2 Batch Sludges

	Gravity Thickening		Air Flotation Thickening		Centrifugation		Vacuum (pressure) Filtration		Aerobic Digestion		Anaerobic Digestion Primary		Anaerobic Digestion Secondary		Wet Air Oxidation	
	F[1]	L[2]	F	L	F	L	F	L	F	L	F	L	F	L	F	L
Temperature									I/D	Is	Mn	Is	Mn	Is	Mn	Is
pH									I/D	Is	I/D	Is			I/D	S
BOD	2/W	Su	2/W	Su	I/W	C	2/W	F	AD	S			I/W	S	2/D	S
SS	I/D	Su	I/D	Su	I/D	C	I/D	F	AD	S			I/W	S	I/D	S
TS	I/D	I P	I/D	I P	I/D	I P	I/D	I P	2/W	I P	I/W	Is	AD	U	I/D	I U
TVS									2/W	I P	I/W	Is	AD	U		
Alkalinity											I/D	Is				
Volatile Acids											2/W	I				
Settleable Solids					I/H	C			3/W	Is						

1. F = frequency
2. L = location

where:

Mn = monitor
H = hour
D = day
W = week

AD = at drawoff
Su = subnatant
I = influent
P = product sludge or cake
C = centrate
F = filtrate
Is = in situ
S = supernatant or decant
U = underflow

Figure 9.1 Recommended minimum sampling programs for municipal wastewater sludge treatment processes (2)

9.4.2.1 Digesters - Collect samples from a mixed sink which is fed through lines attached at different levels in the digester. Be certain to waste sludge accumulated in the lines prior to sampling (1).

9.4.2.2 Tanks - Mix tank thoroughly and collect samples. Or collect samples at various depths and locations in the tank. Mix samples together prior to analysis.

9.4.3 Specific "In Plant" Locations

The following locations are recommended for sludge sampling at wastewater treatment plants:

1. Primary Sludge - Draw sludge from the settling tank hoppers into a well or pit before pumping, mix well and then collect a representative sample directly from this well. Alternately, collect samples from openings in pipes near the sludge pumps or from the pump itself (4).

2. Activated Sludge - Collect samples at:

   a. the pump suction well
   b. the pump or adjacent piping
   c. the point of discharge of the return sludge to the primary effluent.

   The sample point should be located in a region of good agitation to insure suspension of solids (4).

3. Digested Sludge - Collect samples at the point of the discharge of the digester drawoff pipe to the drying beds or the drying equipment (3).

4. Bed Dried Sludge - Collect equal-sized samples at several points within the bed without including sand. Mix thoroughly (4).

5. Filtered Sludge - Collect equal size portions (possibly by using a cookie cutter) at the filter discharge (4).

9.5 FREQUENCY OF SAMPLING

The extreme variability of sludges creates a need for frequent sampling to achieve accurate results. Each composite sample should be composed of at least 3 individually obtained samples (4). Sample batch operations at the beginning, middle and end of a discharge, or more frequently if high variability is suspected (4). Tapped lines should also be sampled in three separate intervals because of variations in the sludge at the drawoff source (i.e., clarifier, digester, etc.). Minimum frequencies for various sludge processes

are included in Figure 9.1.

9.6 NUMBER OF SAMPLES

The number of samples is determined from the frequency and the number to include in the composite. Refer to Figure 9.1 for minimum guidelines.

9.7 TYPE OF SAMPLE

Collect grab samples when analyzing an unstable sludge for a parameter which is affected by the instability, or when analysis is required as soon as possible (e.g., sludge volume index test for activated sludge samples).

Analysis of composite samples is recommended in all other situations to reduce the effects of sludge variability. Use at least three individual samples to form the composite. Wherever possible, collect frequent discrete samples and composite according to flow rate (5).

9.8 METHOD OF SAMPLING

Automatic samplers are not commonly available for sludge sampling due to the high fouling potential and solids content of the wastewater. Use manual sampling techniques in most situations unless special adaptations can be made.

9.9 VOLUME OF SAMPLE AND CONTAINER TYPE

Use a wide mouth container to sample sludges. The size and material of container depends on the parameters to be analyzed. In general, a clean borosilicate glass container is preferable to reduce the possibility of adsorption of organics to the container wall; however, polyethylene can be used. See Chapter 10 for more details.

9.10 PRESERVATION AND HANDLING OF SAMPLES

Preservation methods are discussed in Chapter 10. Be certain to completely mix the sample after a preservative is added to disperse the chemical and allow adequate preservation. Considerable mixing or homogenization is required prior to aliquot removal to insure representative portions are obtained. Further studies on the preservation of sludges appear warranted.

9.11 FLOW MEASUREMENT

For flowing lines do not use flow measuring devices which will be easily fouled by solids (e.g., orifice, venturi meter). Use a permanently installed, self-cleaning or non-obstructive device such as a magnetic flow meter.

Batch sludge discharges are not easily quantified in terms of volume discharged. Make estimates from pump capacity, the change in depth in a tank or well and time of pumping or other appropriate methods.

9.12 REFERENCES

1. Joint Committee of American Society of Civil Engineers and Water Pollution Control Federation. Sewage Treatment Plant Design - WPCF Manual of Practice, No. 8, 1967.

2. Estimating Laboratory Needs for Municipal Wastewater Treatment Plants. USEPA, Office of Water Program Operations, Washington, D.C., Report No. EPA-430/9-74-002. Operation and Maintenance Program. June 1973, pp. A-1 to A-29.

3. Technical Practice Committee - Subcommittee on Operation of Wastewater Treatment Plants. Operation of Wastewater Treatment Plant - WPCF Manual of Practice No. 11, 1970.

4. New York State Department of Health. Manual of Instruction for Sewage Treatment Plant Operators, New York, N.Y., Health Education Service, 308 p.

5. Technical Practice Committee - Subcommittee on Sludge Dewatering. Sludge Dewatering - WPCF Manual of Practice No. 20, 1969.

CHAPTER 10

SAMPLE PRESERVATION AND HANDLING BY PARAMETER GROUP

10.1 INTRODUCTION

Sample preservation is distinctive to each parameter so recommendations have been divided into individual categories. The parameter groups in Table 10.1 are covered in this chapter. Microbiological parameters are covered in Chapter 11.

Certain precautions and considerations are necessary when applying these recommendations:

1. An asterisk is used when insufficient information is available for recommendations and the best available technique has been included.

2. When a chemical preservative is added to sludge or high solids concentration samples, extreme agitation is necessary to disperse the chemical preservative throughout the sample. If the chemical preservative cannot be dispersed, the alternate preservation method must be used.

3. Holding times are divided into two sections to reduce the problems arising when composite samples are analyzed. The maximum compositing interval is applicable in situations when a chemical preservative is needed but is not added until after the composite is complete.

Whenever possible an alternate procedure using refrigeration only has been included with a shorter holding time. Use this approach when the recommended preservative may interfere with some of the analysis.

10.2 METHODS FOR NUTRIENTS PARAMETER GROUP

10.2.1 Background

In terms of the materials necessary to support aquatic plant and animal life "nutrients" is a broad term. However, for this report it should

Table 10.1. PARAMETER GROUP CLASSIFICATIONS

CHEMICAL PARAMETER GROUPS

Nutrients	Demand	Metals		Physical/Mineral		Pesticides and Others
Kjeldahl Nitrogen	BOD	Arsenic	Beryllium	Acidity	Specific Conductance	DDT
Ammonia Nitrigen	COD	Boron	Cakium	Alkalinity	Sulfide	Dieldrin
Nitrate-Nitrogen	TOC	Chromium	Magnesium	Bromide	Sulfite	PCB's
Nitrite-Nitrogen	DO	Mercury	Potassium	Chloride	Sulfactants	Benzidine
Ortho Phosphate		Sodium	Aluminum	Chlorine	Total Solids	Algicides
Total Phosphate		Antimony	Barium	Color	Suspended Solids	
		Cobalt	Cadmium	Cyanide	Volatile Solids	
		Copper	Lead	Fluoride	Total Dissolved Solids	
		Iron	Nickel	Hardness	Turbidity	
		Zinc	Vanadium	Oil and Grease		
		Manganese	Molybdenum	pH		
		Selenium	Silver	Phenols		
		Thallium	Tin			
		Titanium				

Radioactive Materials	Biological
Alpha	Benthic Macroinvertebrates
	Fish
Beta	Macroalgae
Radium	Macrophyton
	Periphyton
	Phytoplankton
	Zooplankton

be understood that the term refers to the common nitrogen and phosphorus forms. Both nitrogen and phosphorus can be limiting factors in the growth of aquatic life. Both nitrogen and phosphorus are present in large quantities in many of the inputs to surface waters such as wastewater treatment plant effluent and agricultural runoff.

10.2.1.1 Nitrogen compounds - Nitrogen occurs in natural systems in as many as seven valence states. Of these, four are of major interest in environmental applications: total Kjeldahl nitrogen, ammonia, nitrate and nitrite. These compounds are readily interconverted by bacterial action, and the ratios of concentrations can be used as an indication of recent pollution. The total Kjeldahl nitrogen includes ammonia, polypeptides, amino acids and other long chain organonitrogen compounds. These organics can be changed into ammonia plus other compounds by certain bacteria. The ammonia can then be converted to the nitrite state, hydrogen ions and water by other bacteria under aerobic conditions. However, nitrite is quite unstable and can be easily converted to the nitrate form when oxygen is present. The nitrate form is the completely oxidized state of nitrogen and is used as a fertilizer. Nitrates are also contributed from atmospheric nitrogen which is changed to nitric acid anhydride during electrical storms. This unstable form changes to nitric acid upon contact with water. Usually nitrate is present in drinking water at levels of 10 mg/l or less. A limit of 45 mg/l has been established since nitrate causes an illness in infants, known as methemoglobinemia (1).

10.2.1.2 Phosphate compounds - Phosphate is present in natural systems in three forms: ortho, condensed, and organic phosphate. It has been found to be a limiting factor in plant growth in concentrations of 10 μg/l (1). The largest contribution of phosphates is now the phosphate based detergents. However, in some instances phosphate is added to a waste, generally an industrial waste, to allow sufficient bacterial growth. Because of its role in the eutrophication of lakes, the phosphorus concentration in point discharges to such bodies of water is being closely monitored.

10.2.2 Recommended Preservation and Handling Methods

10.2.2.1 General - The use of mercuric chloride and sulfuric acid have been found to be effective in preserving most nutrient types (2,3, 4,5,6). Although the 1971 EPA Methods Manual among others (7) suggests a dosage of 40 mg/l mercuric chloride, studies by Krawczyk (6), Hellwig (3) and Howe and Holley (5) indicated higher dosages were necessary in polluted water. The adverse environmental effect of mercury must be considered. If this toxic preservative is added in the field there is a danger of environmental contamination; even lab disposal by normal procedures can result in indirect contamination by dilute mercury in water. Therefore, whenever other preservatives are available and

adequate, they should be used and mercuric chloride avoided. When sulfuric acid is used as a preservative, reduce the pH of the sample to 1.5. Studies have shown that this level must be reached for effective bacterial kills (8). TBS Prakasam showed that acid addition to pH 2 will still allow the ammonia content of a sample to increase indicating that bacterial activity still existed (9). However, whenever possible acid should be used in preference to mercury, although both methods are acceptable. When mercury is used, samples must be treated for mercury reclamation using the procedure in Section 10.2.2.2.

10.2.2.2 Mercury Reclamation - In order to use mercury salt solutions as preservatives, the mercury solution must be cleaned prior to disposal. The recommended procedure allows the collection of mercuric chloride on an Amberlite IRA-400 resin. The system is then regenerated and the collected regenerant sent to a mercury reprocessor. There are several reprocessers available nationally some of whom are listed in Table 10.2.

A summary of the procedure to be used follows (11):

1. Adjust the pH of highly acidic solutions to pH of 4-6 and highly basic solutions to pH of 6-8. Solutions originally in the range of 6-8 are not to be adjusted.

2. Settle sample 24 hours to allow precipitates to form and settle.

3. Vacuum filter solutions through a large bench top Buchner funnel (approximately 32 cm in diameter) using relatively fast paper.

4. Add 5 mg/l sodium chloride solution to the filtrate to form the $HgCl_4^{-2}$ complex anion. This amount of NaCl will complex up to 400 mg/l of Hg in solution.

5. Pass the treated solution through a glass column (3 1/2 in 10 x 4 in OD x 4 ft high) containing a bed of the ion exchange resin IRA-400 three feet deep topped off with a bed of activated charcoal 6-8 in. deep at a rate of flow of 500 ml/min.

10.2.2.3 Total Kjeldahl Nitrogen - Use sulfuric acid (preferred) or chloride (only if necessary) plus refrigeration to preserve samples for Kjeldahl nitrogen analysis. Samples can be held up to 30 days (12) when sulfuric acid is used and up to 42 days (13) with mercuric chloride. Clean borosilicate glass containers as indicated in Section 3.4 but no special preparation is necessary. Ice the samples during the compositing period and add the total chemical preservative prior to sample collection or immediately after the composite is formed. The volume needed varies with the analytical method. If a macro Kjeldahl digestion is done, collect 500-800 mls of sample depending upon the expected concentration, collect 20-100 mls if a Technicon or automated

Parameter: Total Kjeldahl Nitrogen (Primary)

Water or Wastewater: x Municipal Wastewater x Agricultural Runoff

x Industrial Wastewater x Sludge*

x Surface Water x Sediment*

Preservation Method: Preferred: add H_2SO_4 to pH less than 1.5 plus refrigeration at 4°C. Option (not preferred): 40 mg/l $HgCl_2$ plus refrigeration for ocean, surface and mildly polluted waters (TOC<20 mg/l) (6) or 400 mg/l $HgCl_2$ plus refrigeration for highly polluted waters (TOC>20 mg/l)

Maximum Holding Times

Grab Samples 30 days

Composite Samples (After Composite Preparation) 29 days Max. Compositing Period 24 hours

Container Type: Glass or plastic

Volume: 500-800 mls (maxi analysis) or 20-100 mls (automated analysis)

Preparation Method: none

Comments: Add preservative prior to sample collection/ice during compositing. Use fulfuric acid whenever possible.

Parameter: Total Kjeldahl Nitrogen (Alternate)

Water or Wastewater: x Municipal Wastewater x Agricultural Runoff

x Industrial Wastewater x Sludge *

x Surface Water x Sediment*

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 6 hours* Max. Compositing Period 24 hours

Container Type: Glass or plastic

Volume: 500-800 mls

Preparation Method: none

Comments: --

Figure 10.1. Recommended preservation and handling methods - TKN

Table 10.2. PARTIAL LISTING OF COMMERCIAL MERCURY REPROCESSORS (10)

Company	Processing [a]
Bethlehem Apparatus Co., Inc. Front and Depot Streets Hellertown, PA 18055 Phone: (215) 838-7034	M
Goldsmith Division, National Lead Co. 111 North Wabash Chicago, IL 60602 Phone: (312) 726-0232	M
Mallinckrodt Chemical Works 223 West Side Avenue Jersey City, NJ 07303 Phone: (201) 432-2500 (Mr. Frank L. Mackey, Eastern Branch Plant Manager)	M C O
Quicksilver Products, Inc. 350 Brannan Street San Francisco, CA 94107 Phone: (415) 781-1988 (Miss Grace Emmans, Owner and President)	M C
Sonoma Mines, Inc. P.O. Box 226 Guerneville, CA 94556 Phone: (707) 869-2013 (Mr. C. O. Reed, President)	C
Wood Ridge Chemical Corp. Park Place East Wood-Ridge, NJ 07075 Phone: (201) 939-4600 (Mr. E. L. Cadmus, Technical Director)	M C

[a] M = Supplies flasks for return of metallic mercury.

C = Will accept mercury sulfide for reprocessing.

O = Will accept certain organic mercury chemicals.

Special approval must always be obtained before shipment is made to a reprocessor.

technique is to be used. Follow the sampling procedures outlined in Section 2.5.

10.2.2.4 Ammonia Nitrogen - Use sulfuric acid (preferred) or mercuric chloride plus refrigeration to preserve ammonia samples. Avoid extended exposure to the air (14,15) by keeping the container capped. The holding time depends on the type of sample. If a raw sewage sample is to be analyzed, hold up to seven days and if other, less polluted samples are involved a holding time up to 30 days in acceptable when sulfuric acid is the preservative (12). The maximum compositing period is 24 hours with icing of the samples during this interval. The preservative should be added to the container prior to sample collection or immediately after the composite is formed. Collect 500-800 mls of sample volume into glass or polyethylene bottles when macro analysis is necessary. If the Technicon or automatic analysis is used the required volume is 20-100 mls. Clean the container as indicated in Section 3.4; no special precautions are necessary.

10.2.2.5 Nitrate Nitrogen* - Mercuric chloride plus refrigeration at 4°C is the only acceptable preservative since acid catalyzes the nitrite to nitrate conversion (4). Referenced holding times vary from 18 to 100 days (3,5,6,16). Therefore an 18 day holding time is recommended until further study is done. Turbidity removal may be required prior to analysis. Clean borosilicate glass or polyethylene containers as indicated in Section 3.4. Collect a 100-250 ml volume of sample following the procedures outlined in Section 2.5.

10.2.2.6 Nitrite Nitrogen - Same as nitrate nitrogen but use 7 day holding time.

10.2.2.7 Total Nitrate/Nitrite Nitrogen - Preserve the total nitrite/nitrate group by addition of sulfuric acid when possible since interconversion of the species is not critical. Mercuric chloride can be used but is not preferred. Hold samples after preservation and refrigeration at 4°C for up to 30 days (12). Collect a 100-250 ml volume of sample into borosilicate glass or polyethylene containers. No special preparation is required, but clean containers as indicated in Section 3.4. Collect samples as outlined in Section 2.5 with no special provisions.

10.2.2.8 Ortho Phosphate - Immediately after collection, filter samples through washed 0.45 μ membrane (17) filters into an acid washed borosilicate glass container (18). This procedure will reduce the conversion of condensed phosphate to ortho phosphate by removing suspended and microbial material which may catalyze the reaction (17). Do not add sulfuric acid because this will hasten the hydrolysis of compounds (19, 20). Refrigerate the samples at 4°C or lower and analyze immediately if possible or within 48 hours. Do not collect automatic composite samples for orthophosphate analysis because the sample cannot be immediately filtered and the transfer of the sample may cause adsorbance to container walls to be more critical. If unfiltered samples are analyzed, then the data record

Parameter: Ammonia Nitrogen (Primary)

Water or Wastewater:

X	Municipal Wastewater	X	Agricultural Runoff
X	Industrial Wastewater	X	Sludge *
X	Surface Water	X	Sediment *

Preservation Method: Preferred: Add H_2SO_4 to pH less than 1.5 plus refrigeration at 4°C. Option (not preferred): 40 mg/l $HgCl_2$ plus refrigeration for ocean, surface and mildly polluted waters (TOC<20 mg/l)(6) or 400 mg/l $HgCl_2$ plus refrigeration for highly polluted waters (TOC>20 mg/l)

Maximum Holding Times

Grab Samples 7 days for strongly polluted water (Raw sewage)
30 days for mildly polluted water (Low biological activity)

Composite Samples (After Composite Preparation) 6-29 days Max. Compositing Period 24 hours
(See grab restrictions)

Container Type: Glass or Plastic

Volume: 100-1000 mls for manual method or 20-100 mls for automated analysis

Preparation Method: None

Comments: Use H_2SO_4 whenever possible/ice the sample during compositing

Parameter: Ammonia Nitrogen (Alternate)*

Water or Wastewater:

X	Municipal Wastewater	X	Agricultural Runoff
X	Industrial Wastewater	X	Sludge *
X	Surface Water	X	Sediment *

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 6 hours* Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 100-1000 mls (20-100 mls for automated analysis)

Preparation Method:

Comments: Ice sample during compositing

Figure 10.2 Recommended preservation and handling methods-NH_3

Parameter: Nitrate Nitrogen (Primary)

Water or Wastewater:

X	Municipal Wastewater	X	Agricultural Runoff
X	Industrial Wastewater	X	Sludge
X	Surface Water	X	Sediment

Preservation Method: Preferred: Add H_2SO_4 to pH less than 1.5 plus refrigeration at 4°C. Option (not preferred): 40 mg/l $HgCl_2$ plus refrigeration for ocean, surface and mildly polluted waters (TOC<20 mg/l)(6) or 400 mg/l $HgCl_2$ plus refrigeration for highly polluted waters (TOC>20 mg/l)

Maximum Holding Times

Grab Samples 18 days (5)

Composite Samples (After Composite Preparation) 17 days (5) Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 100-250 mls.

Preparation Method: Turbidity Removal

Comments: Acid catalyzes conversion of nitrite to nitrate (4)

Parameter: Nitrate Nitrogen (Alternate)

Water or Wastewater:

X	Municipal Wastewater	X	Agricultural Runoff
X	Industrial Wastewater	X	Sludge*
X	Surface Water	X	Sediment*

Preservation Method: Refrigerate at 4°C

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 6 hours* Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 100-250 mls

Preparation Method: Turbidity Removal

Comments:

Figure 10.3. Recommended preservation and handling method-NO_3

Parameter: Nitrite Nitrogen (Primary)

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff

X Industrial Wastewater X Sludge*

X Surface Water X Sediment*

Preservation Method: Preferred: Add H_2SO_4 to pH less than 1.5 plus refrigeration at 4°C. Option (not preferred): 40 mg/l $HgCl_2$ plus refrigeration for ocean, surface and mildly polluted waters (TOC<20 mg/l)(6) or 400 mg/l $HgCl_2$ plus refrigeration for highly polluted waters (TOC>20 mg/l)

Maximum Holding Times

Grab Samples 11 days

Composite Samples (After Composite Preparation) 10 days Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 100-250 mls

Preparation Method: Turbidity Removal

Comments: Acid catalyzes conversion of nitrite to nitrate (4).

Parameter: Nitrite Nitrogen (Alternate)

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff

X Industrial Wastewater X Sludge*

X Surface Water X Sediment*

Preservation Method: Refrigerate at 4°C

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 6 hours* Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 100-250 mls

Preparation Method: Turbidity Removal

Comments:

Figure 10.4. Recommended preservation and handling method-NO_2

Parameter: Total Nitrite/Nitrate Nitrogen

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff

X Industrial Wastewater X Sludge *

X Surface Water X Sediment *

Preservation Method: Preferred: Add H_2SO_4 to pH less than 1.5 plus refrigeration at 4°C. Option (not preferred): 40 mg/l $HgCl_2$ plus refrigeration for ocean, surface and mildly polluted waters (TOC<20 mg/l)(6) or 400 mg/l $HgCl_2$ plus refrigeration for highly polluted waters (TOC>20 mg/l)

Maximum Holding Times

Grab Samples 30 days (12)

Composite Samples (After Composite Preparation) 29 days Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: - 100-250 mls

Preparation Method: None

Comments: Use H_2SO_4 whenever possible

Figure 10.5. Recommended preservation and handling methods-NO_2/NO_3

Parameter: Ortho Phosphate (Primary/No Alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff

X Industrial Wastewater X Sludge *

X Surface Water X Sediment *

Preservation Method: Filter immediately after sampling through 0.45μ membrane filters and refrigerate at 4°C

Maximum Holding Times

Grab Samples Immediately to 48 hours (maximum)*

Composite Samples (After Composite Preparation) Not recommended Max. Compositing Period --

Container Type: Boroslicate glass/acid washed

Volume: 50-250 ml

Preparation Method: Immediate filtration 0.45μ

Comments:

Figure 10.6. Recommended preservation and handling method - Ortho Phosphate

must indicate this fact. Acid wash borosilicate glass containers with a hydrochloric acid mixture as indicated in Section 3.4 after the container has been cleaned. Collect 50-250 ml of sample using the grab sampling precautions listed in Section 2.5.

10.2.2.9 Total Phosphate - Add sulfuric acid (preferred) or mercuric chloride to preserve samples for total phosphate analysis. Use acid when only phosphate is analyzed or when it does not interfere with other analyses. Use mercuric chloride when interference is involved to reduce the rate of degradation in the sample (16). Samples are stable and can be held indefinately (12, 16). Rinse borosilicate glass or polyethylene containers with hydrochloric acid (see Section 3.4) after cleaning. This procedure will remove detergent or other residual phosphates (18). Collect 50-250 ml samples as composite or grab samples following the recommendations in Section 2.5.

10.2.2.10 Preservation For All Nutrients - Collect two samples if all nutrients are analyzed. Use one borosilicate glass or polyethylene container which has been previously hydrochloric acid rinsed to collect 2550 ml of sample or 1000 mls if automated analysis of ammonia and TKN is used. Follow grab or composite procedures indicated in Section 2.5. Add mercuric chloride and refrigerate samples. These samples can be held 7 to 30 days. This procedure will be sufficient for TKN, ammonia, nitrate, nitrite and total phosphate. Collect a second sample of approximately 250 ml, filter (0.45 μ membrane) into a hydrochloric acid rinsed borosilicate glass bottle and refrigerate at 4°C. Analyze this sample for orthophosphate within 48 hours of sampling.

10.3 METHODS FOR DEMAND PARAMETER GROUP

10.3.1 Background

The uptake of oxygen is critical to many life forms. Since a suitable amount of dissolved oxygen is needed for most aquatic life to exist, the importance of demand cannot be minimized. Since dissolved oxygen is inherently related to this overall measure, this parameter has also been included in this section.

10.3.1.1 Biochemical Oxygen Demand (BOD) - One way of measuring the impact of a discharge on a receiving stream is by analysis of biochemical oxygen demand. This procedure is generally a bioassay technique which measures the amount of oxygen used by organisms aerobically decomposing organic material. In general, standard conditions are used to simulate a biological environment. Samples are seeded with a varied culture of microorganisms, diluted with nutrient rich water (in some cases), and incubated in the dark at 20°C for 5 days. After this time the oxygen concentration is again measured. The depletion is said to represent 70-80 percent of the total demand for a domestic waste. The oxygen used

Parameter: Total Phosphate (Primary)

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge *
X Surface Water X Sediment *

Preservation Method: H_2SO_4 to pH < 1.5 plus refrigeration at 4^oC or
40 to 400 mg/l $HgCl_2$ plus refrigeration at 4^oC

Maximum Holding Times

Grab Samples Indefinite (12)

Composite Samples (After Composite Preparation) Indefinite Max. Compositing Period 24 hours

Container Type: Glass or Plastic/ Hydrochloric Acid Wash

Volume: 50-250 mls - depends on concentration

Preparation Method: None

Comments: Use acid whenever possible

Parameter: Total Phosphate (Alternate)

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge*
X Surface Water X Sediment*

Preservation Method: Refrigerated at 4^oC

Maximum Holding Times

Grab Samples Indefinite

Composite Samples (After Composite Preparation) Indefinite Max. Compositing Period 24 hours

Container Type: Glass or Plastic/ Hydrochloric Acid Wash

Volume: 50-250 ml

Preparation Method: --

Comments: --

Figure 10.7. Recommended preservation and handling methods-Total Phosphate

is theoretically related to the organic concentration by the following equation.

$$C_n H_a O_b N_c + (n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4} c)\ O_2 \longrightarrow n\ CO_2 + (\frac{a}{2} - \frac{3}{2} c)\ H_2O + cHN_3$$

However, precision varies [up to 20% reproducibility(1)] according to many factors including toxic substances, critical concentrations, initial conditions, acclimation and others. Another disadvantage of the BOD parameter is the length of time (at least 5 days) between sample collection and reporting of the test results.

10.3.1.2 Chemical Oxygen Demands (COD) - This test measures the total amount of oxidizable matter under acidic oxidizing conditions. It is imperative that exactly the same procedure by followed for all analyses because the extent of reaction is time and temperature dependent. The disadvantage of the COD parameter is that it may not be indicative of the biochemical oxygen demand in an environment. Either materials are oxidized in the COD test which are not biologically attacked or chemical species such as sulfite create excessive oxygen depletions. This may result in misrepresentation of the biochemical oxygen demand. However, the test results can be obtained within three hours.

10.3.1.3 Total Organic Carbon (TOC) - The total organic carbon can be related to the oxygen demand by the equation: $C + O_2 \longrightarrow CO_2$. However, compounds which contain oxygen are not adequately represented using this formula and partial oxidation is not measured (i.e., acetaldehyde and oxygen to acetic acid). The same problem exists for this test as for COD, in that the actual biological effects on the environment are not measured. However, this analysis can be done in minutes and is adaptable to on-line monitoring.

10.3.1.4 Dissolved Oxygen (DO) - The basic objective of all the demand tests is to determine the effect of a discharge on the dissolved oxygen concentration of a receiving water. Often it is desirable to measure or monitor the DO in the receiving water directly. All gases soluble in water are affected by the ambient temperature and pressure and this is also true for oxygen. As the temperature increases, the amount of soluble oxygen decreases. Therefore, the worse conditions are apparent on a hot day. Although the solubility of the oxygen in the atmosphere varies from 7-13 mg/l, 8 mg/l is generally considered the upper limit for demand considerations because of the temperature and altitude dependence.

10.3.2 Recommended Preservation and Handling Methods

10.3.2.1 General - Refrigeration is recommended when biological species are involved while chemical addition can be used when chemical species are considered. Dissolved gases can not be preserved, so *in situ* analysis is required.

10.3.2.2 Biochemical Oxygen Demand - Ice all samples for BOD analysis during collection and transport. Reducing the temperature to the lowest level without freezing is preferable (21). Generally ice is used. Analyze grab samples within 24 hours of collection (22,23). Composite samples can be held an additional 6 hours to allow for transportation of a 24 hour composite sample to the laboratory. Be certain samples are iced during collection (1) and transportation (23). Collect 1 to 2 liters of sample into clean borosilicate glass or polyethylene containers. Follow procedures in Section 2.5 for sample collection.

10.3.2.3 Chemical Oxygen Demand - Add sulfuric acid to achieve a pH of 1.5 (8) and refrigerate the sample at 4°C. Hold the sample up to 7 days. If acid addition affects the stability of the sample refrigerate and analyze within 24 hours (21, 22). This will alleviate the difficulty of deemulsifying an oil and then resuspending it prior to analysis. Homogenize samples with high solids content prior to aliquot removal. Clean glass borosilicate glass or polyethylene containers as outlined in Section 3.4. No special preparation is required. Sample following the procedures in Section 2.5.

10.3.2.4 Total Organic Carbon - Treat the sample the same way as COD (Section 10.3.2.3). Homogenization and ultrafine homogenization may be required prior to analysis if high solids samples are to be analyzed. This will allow removal of representative subsamples and may aid the analytical procedure.

10.3.2.5 Dissolved Oxygen - Analyze DO *in situ* or on the site of sampling. Use the membrane electrode probe calibrated for temperature and altitude whenever possible to minimize interference from pressure and temperature changes and avoid the high alkalinity from the azide technique. Always use a stirring device with a probe to move water past the membrane. If the sample cannot be analyzed *in situ* use glass BOD bottles to contain the sample and eliminate entrained air (1). If transportation prior to analysis is mandatory, fix sample with azide reagents, store at a temperature below that of the water body and analyze immediately upon arrival at the destination. Do not hold sample longer than 4-8 hours (1).

10.3.2.6 Recommended Methods for Entire Group - Take two samples when possible and analyze one immediately for DO or fix with azide analysis for later analysis. Split the second sample into 2 containers (either polyethylene or borosilicate glass). Preserve one bottle, 600 mls, with sulfuric acid to pH less than 1.5 and ice the second bottle, 2 liters, for immediate transport. When the samples arrive at the laboratory, BOD analysis should begin immediately and the pH of the second sample checked to maintain the desired level.

Parameter: Biochemical Oxygen Demand (Primary)

Water or Wastewater:

X	Municipal Wastewater	X	Agricultural Runoff
X	Industrial Wastewater	X	Sludge *
X	Surface Water	X	Sediment *

Preservation Method: Icing at 0°-$4^{o}C$ (Do not freeze)

Maximum Holding Times

Grab Samples 24 hours

Composite Samples 6 hours* (After Composite Preparation) Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 1000-2000 mls

Preparation Method:

Comments:

Parameter: Biochemical Oxygen Demand (Alternate)

Water or Wastewater:

X	Municipal Wastewater	X	Agricultural Runoff
X	Industrial Wastewater	X	Sludge *
X	Surface Water	X	Sediment *

Preservation Method: Refrigeration at $4^{o}C$

Maximum Holding Times

Grab Samples 24 hours (time specified)

Composite Samples 6 hours (time spec.)* (After Composite Preparation) Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 1000-2000 mls

Preparation Method: --

Comments: --

Figure 10.8. Recommended preservation and handling methods-BOD

Parameter: Chemical Oxygen Demand (Primary)

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge*
X Surface Water X Sediment *

Preservation Method: H_2SO_4 to ph less than 2 plus refrigerate at 4^oC

Maximum Holding Times

Grab Samples 7 days* (can be longer if proven)

Composite Samples (After Composite Preparation) 6 days Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 100-500 ml

Preparation Method: Homogenize high solids samples

Comments: --

Parameter: Chemical Oxygen Demand (Alternate)

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge*
X Surface Water X Sediment*

Preservation Method: Regrigeration at 4^oC

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 6 hours* Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 100-500 mls

Preparation Method: Homogenize high solids samples

Comments: Method used if acidification disturbs the stability of the sample

Figure 10.9. Recommended preservation and handling methods - COD

Parameter: Total Organic Carbon (Primary)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge *
X Surface Water X Sediment *

Preservation Method: H_2SO_4 to pH less than 1.5 plus refrigeration at 4oC

Maximum Holding Times

Grab Samples 7 days

Composite Samples (After Composite Preparation) 6 days Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 50 mls

Preparation Method: Homogenization of high solids samples

Comments:

Parameter: Total Organic Carbon (Alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge *
X Surface Water X Sediment *

Preservation Method: Refrigeration at 4^oC

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 6 hours* Max. Compositing Period 24 hours

Container Type: Glass or Plastic

Volume: 50 mls

Preparation Method: Homogenization of high solids samples

Comments: Use alternate when sample contains appreciable amounts of emulsified oil

Figure 10.10. Recommended preservation and handling methods-TOC

Parameter: Dissolved Oxygen (Primary)

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater ___ Sludge
X Surface Water ___ Sediment

Preservation Method: None

Maximum Holding Times

Grab Samples In situ

Composite Samples (After Composite Preparation) Not recommended Max. Compositing Period --

Container Type: Glass - BOD Bottle

Volume: 300 ml

Preparation Method: --

Comments: Do not use electrode on samples with sulfur compounds or on solids

Parameter: Dissolved Oxygen (Alternate)

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge*
X Surface Water X Sediment*

Preservation Method: Fix using Method 4.5.1 or 4.5.2 p 5 greater than 1974 EPA Manual and store at temperature lower than sampling temperature.

Maximum Holding Times

Grab Samples 4-8 hours

Composite Samples (After Composite Preparation) Not recommended Max. Compositing Period --

Container Type: Glass BOD Bottle/Water seal

Volume: 300 ml

Preparation Method: --

Comments: Not used for: raw sewage, biolonical flecs, high solids samples, oxidizing constituents, colorinterferences

Figure 10.11. Recommended preservation and handling methods - DO

10.4 METHODS FOR METALS PARAMETER GROUP

10.4.1 Background

Metals analyses have been greatly simplified by the acceptance of atomic absorption as the major analytical tool. Since metals are often found in very low concentrations, this analytical method is appropriate because of its high sensitivity (see Table 10.3). The metals listed are included in this portion of the report with the addition of boron which is not analyzed using atomic absorption.

10.4.2 Recommended Preservation and Handling Methods

10.4.2.1 Arsenic - Handle arsenic sample without consideration of the analytical technique to use. Collect samples as indicated in Section 2.5 into borosilicate glass or polyethylene bottles previously nitric acid rinsed (see Section 3.4). Collect 100-200 ml and preserve with nitric acid to pH less than 2 to reduce adsorption of ions to the container sides. Store sample a maximum of 6 months but a shorter time is desirable.

10.4.2.2 Boron - Collect 50-100 mls of sample into nitric acid rinsed polyethylene containers (borosilicate containers cannot be used). Refrigerate at 4°C and hold samples up to 6 months.

10.4.2.3 Calcium, Potassium and Sodium - Collect samples of all water or wastewater type and preserve with nitric acid to pH less than 2. The analytical technique does not affect the preservation method. Use nitric acid rinsed polyethylene or borosilicate glass containers (see Section 3.4) and collect 100-250 ml per metal. Hold samples a maximum of 6 months.

10.4.2.4 Chromium VI - Analysis for this unstable metal form should begin immediately (1). If this is not possible, refrigerate the sample and analyze within 24 hours. Ice composite samples over the maximum composite interval of 24 hours and analyze within 6 hours of composite preparation. Report total time between collection and analysis with the results if it exceeds the maximum recommended. Unscratched polyethylene or borosilicate glass containers are required since chromium VI is easily adsorbed to container walls. Acid rinse containers with nitric acid before sample collection. A 100-200 ml volume is sufficient for analysis.

10.4.2.5 Mercury - Preserve samples by adding 5% nitric acid V/V and 0.05% V/V potassium dischromate (26). Nitric acid rinse (see Section 3.4) borosilicate glass or polyethylene bottles. Mercury is much less stable than other metals, so hold samples up to 30 days (12). Only manual grab or manual composite samples are acceptable for mercury analysis due to possible losses of volatile mercury ion. Collect sample (200-300 mls) and preserve immediately. Check nitric acid prior to use for trace mercury content and correct the final result for volume change.

Table 10.3. ATOMIC ABSORPTION CONCENTRATION RANGES WITH CONVENTIONAL ATOMIZATION (25)

Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l		
Aluminum	0.1	1	5	–	100
Antimony	0.2	0.5	1	–	40
Arsenic*	0.002	–	0.002	–	0.02
Barium	0.03	0.4	1	–	20
Beryllium	0.005	0.025	0.05	–	2
Cadmium	0.002	0.025	0.05	–	2
Calcium	0.003	0.08	0.2	–	20
Chromium	0.02	0.1	0.2	–	10
Cobalt	0.03	0.2	0.5	–	10
Copper	0.01	0.1	0.2	–	10
Iron	0.02	0.12	0.3	–	10
Lead	0.05	0.5	1	–	20
Magnesium	0.0005	0.007	0.02	–	2
Manganese	0.01	0.05	0.1	–	10
Mercury**	0.0002	–	0.0002	–	0.01
Molybdenum	0.1	0.3	0.5	–	20
Nickel	0.02	0.15	0.3	–	10
Potassium	0.005	0.04	0.1	–	2
Selenium*	0.002	–	0.002	–	0.02
Silver	0.01	0.06	0.1	–	4
Sodium	0.002	0.015	0.03	–	1
Thallium	0.1	0.5	1	–	20
Tin	0.8	4	10	–	200
Titanium	0.3	2	5	–	100
Vanadium	0.2	0.8	1	–	100
Zinc	0.005	0.02	0.05	–	2

*Gaseous hydride method.

**Cold vapor technique.

Parameter: Arsenic

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge*
X Surface Water X Sediment*

Preservation Method: HNO_3 addition to pH < 2

Maximum Holding Times

Grab Samples 6 months

Composite Samples (After Composite Preparation) 6 months Max. Compositing Period 24 hours

Container Type: Plastic or Glass/HNO_3 Rinse

Volume: 100-200 mls

Preparation Method:

Comments:

Parameter: Boron

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge*
X Surface Water X Sediment*

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 6 months

Composite Samples (After Composite Preparation) 6 months Max. Compositing Period - no maximum -

Container Type: Plastic only/HNO_3 Rinse

Volume: 50-100 mls

Preparation Method: None

Comments: --

Figure 10.12. Recommended Preservation and handling methods-As & B

Parameter: Calcium, Potassium and Sodium

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge *
X Surface Water X Sediment *

Preservation Method: HNO_3 addition to pH less than 2

Maximum Holding Times

Grab Samples 6 months

Composite Samples (After Composite Preparation) 6 months Max. Compositing Period 24 hours

Container Type: 100-250 mls

Volume:

Preparation Method:

Comments:

Parameter: Chromium VI

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge *
X Surface Water X Sediment *

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 12 hours Max. Compositing Period 24 hours

Container Type: Plastic or glass (not scratched)/HNO_3 Rinse

Volume: 100-200 mls

Preparation Method: Remove solids by centrifuge

Comments:

Figure 10.13. Recommended preservation and handling methods-Ca, K, Na, Cr VI

Parameter: Mercury

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge *
X Surface Water X Sediment *

Preservation Method: 5% v/v HNO_3 addition plus 0.05% Cr_2O_7*

Maximum Holding Times

Grab Samples 30 days (12)

Composite Samples (After Composite Preparation) Manual, only 30 day Max. Compositing Period

Container Type: Plastic or Glass/HNO_3 Rinse

Volume: 200-300

Preparation Method: None

Comments: * Correction for volume channe plus analysis of acid for mercury impurities required

Parameter: Silver

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge *
X Surface Water X Sediment *

Preservation Method: HNO_3 addition to pH less than 2

Maximum Holding Times

Grab Samples 30 days

Composite Samples (After Composite Preparation) 30 days Max. Compositing Period 24 hours

Container Type: Polyethylene/ HNO_3 Rinse

Volume: 200-300

Preparation Method: None

Comments:

Figure 10.14. Recommended preservation and handling methods-Hg, Ag

10.4.2.6 Silver - Keep samples for silver analysis in nitric acid rinsed polyethylene containers and store in the dark. Add nitric acid to pH less than 2 to reduce adsorption. Hold samples up to 30 days (27) maximum. Collect a sample volume of 200-300 ml following the procedures in Section 2.5.

10.4.2.7 Other Metals - Take samples for metal analysis in nitric acid washed borosilicate glass or polyethylene containers (28). Collect a volume of 200-500 ml (depending on precision required) using the procedures outlined in Section 2.5. Preserve samples by addition of nitric acid to pH 2 (27). They are stable up to 6 months with preservation. To preserve dissolved parameters, filter sample through 0.45 μ filter paper and add nitric acid to pH less than 2. The filtrate is then stable up to 6 months. These techniques for total metals apply to (25):

Aluminum	Iron	Thallium
Antimony	Lead	Tin
Barium	Magnesium	Titanium
Beryllium	Manganese	Vanadium
Cadmium	Molybdenum	Zinc
Chromium (Total)	Nickel	
Cobalt	Selenium	
Copper	Silver	

10.4.2.8 Preservation Methods for All Metals - Take one 200 ml sample into a nitric acid washed polyethylene bottle. Analyze for chromium VI immediately and place a boron aliquot in separate plastic container. Acidify the remainder with nitric acid to pH 2 and refrigerate up to 6 months. Manually collect the mercury sample and preserve immediately in a separate container with potassium dichromate.

10.5 METHODS FOR PHYSICAL/MINERAL PARAMETER GROUP

10.5.1 Background

The physical and mineral group encompasses a wide range of parameters. To simplify this section, these constituents have been subdivided into anions and other parameters. This subdivision is given below:

Anions	Other	
Bromide	Conductivity	pH
Chloride	Alkalinity	Acidity
Cyanide	Chlorine	Hardness
Fluoride	Oil and Grease	Phenols
Sulfate	Surfactants	Color
Sulfide	Total Solids	Suspended Solids
Sulfite	Dissolved Solids	Volatile Solids
	Turbidity	

Parameter: All Others Total Metals

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff

X Industrial Wastewater X Sludge *

X Surface Water X Sediment *

Preservation Method: HNO_3 addition to pH less than 2

Maximum Holding Times

Grab Samples 6 months

Composite Samples (After Composite Preparation) 6 months Max. Compositing Period 24 hours

Container Type: Plastic or Glass/HNO_3 Rinse

Volume: 200-500 ml

Preparation Method: None

Comments: Dissolved metal samples should be filtered immeidately on site and then nitric acid added to pH less than 2.

Figure 10.15. Recommended preservation and handling methods-Metals

10.5.1.1 Anions - These anions are diverse and found in wide ranges of concentration across the country. Bromide is generally contributed by leaching from sea water but recently industrial discharges have released this compound. However, the normal concentration remains less than 1 mg/l. Chloride, on the other hand, is quite common in all water supplies. Salt passes through the bodies of most organisms virtually unchanged. In domestic wastewater this can add approximately 15 mg/l Cl^- to the waste stream. Chloride can add a salty taste to water in concentrations greater than 250 mg/l. Fluoride was found to be an effective tooth decay preventative in low concentrations (1 mg/l). However, concentrations greater than 10 mg/l can be harmful. The addition of fluoride is carefully monitored so the disadvantages are not apparent.

Cyanide compounds are any material with a CN^- group attached. They can be either simple or complex but are toxic if they solubilize in water. If cyanides are present in water at concentrations as low as 0.1 mg/l, they will adversely affect the biological activity of a natural water body.

The three sulfur compounds, sulfate, sulfite and sulfide are interrelated through bacterial or oxidizing activity. Sulfite, $SO_3^=$, is readily oxidized to sulfate, $SO_4^=$, under aerobic conditions and is therefore very unstable. Sulfate is commonly found in waters and wastewaters but under certain circumstances it can be converted to sulfide causing corrosion and odor. The mechanism for these conversions is as follows:

$$SO_4^= + \text{organic materials} \xrightarrow[\text{bacteria}]{\text{anaerobic}} S^= + H_2O + CO_2$$

$$S^= + 2H^+ \rightleftharpoons H_2S$$

The hydrogen sulfide gas is odorous and the hydrogen ions released with the gas will accumulate in sewers causing crown corrosion. Therefore, the concentrations of parameters in this group are frequently monitored

10.5.1.2 Other Compound and Materials - More information is found regarding the other physical and mineral parameters. However, the amount of information available is dependent on the specific constituent. Specific conductance or conductivity will give a general indication of the ionic concentration of a solution. In most applications, conductance can only be used as a monitoring parameter, rather than an actual indication of concentrations. On the other hand, pH measures the concentration or activity of hydrogen ions. Most potable waters are slightly basic due to the presence of carbonate or bicarbonate, but this may be affected by other constituents. Alkalinity and acidity are related to the buffering capacity of a water or wastewater. Acidity is the capacity of a water or wastewater to donate protons. The corrosiveness of a water

increases at high acidity and there is always some acidity in waters with pH lower than 8.5. Alkalinity is the capacity of water of wastewater to neutralize acids or accept protons. The main contributors to alkalinity are salts of weak acids or strong basic compounds. Both acidity and alkalinity are related to the carbon dioxide - carbonate - bicarbonate interaction in a water system.

Hardness is defined as the capacity of a water to precipitate soap. This is, in most cases, equal to the sum of the calcium and magnesium ion concentrations since other contributing constituents are usually apparent in very low amounts. The amount of hardness is significant from two standpoints. The second effect is the higher pipe scaling occurrence when hard water is used. The following indicates the relative degrees of hardness:

Hardness, mg/l	Classification
0-75	Soft
75-150	Moderately hard
150-300	Hard
300 and up	Very hard

Color and turbidity can often be confused. However, the distinction is that turbidity will affect the passage of light and is caused by suspended matter in the water. It is the property that scatters light and can be caused by any type of material, inorganic to organic. True color is the natural tint of the water after the suspended material has been removed. Apparent color will indicate the turbidity also. In most cases true color is that desired by an investigator. This can be imparted to a water through natural sources or certain industrial discharges.

Chlorine residual is measured on domestic water supplies or wastewaters that have been discharged. The use of chlorine as a disinfectant is widespread and has been studied extensively. There are two mechanisms for chlorine disinfection. One is free chlorine which is defined as chlorine, hypochlorous acid and hypochlorite. The other mechanism is that of combined chlorine or chloramines. Both types should be included when testing total residual chlorine.

Oil and grease are defined as any material which is soluble in extractant. This can include long chain hydrocarbons, fatty acids, esters, oils and other materials. Determination of representative oil and grease is difficult because of its low solubility and tendency to separate from water. Therefore, collection of a representative sample is complicated by oil gathering on the surface of a water body.

Phenols are used in the manufacture of plastics resins and dyes and are discharged from energy related industries. They are present in water in very low concentrations but are offensive because of their acidic character. At concentrations as low as 1 mg/l they impart objectionable tastes and odors to water supplies. Chlorinated phenolics can cause unpleasant effects at concentrations of 1 µg/l.

Surfactants often referred to as methylene blue active substances are a group of materials used as bases for synthetic detergents. The most commonly measured compound is linear alkylate sulfonate (LAS) and this material is the standard compound in analytical tests.

Solids or residue are some of the most commonly measured parameters in laboratories. There are a variety of types of solids including total, suspended, total volatile and total dissolved solids. Total solids is defined as that residue which remains after evaporation and drying at 103-105°C. Suspended solids are those materials which remain on a filter of 0.45 µ membrane or a glass fiber filter. Dissolved solids are those which remain in solution after this filtration. Total volatile solids are those materials which are lost when a solids sample is ignited at 550°C for 20 minutes. The volatile solids are related to the organic content of a sample. The solids content must be low in potable water. Dissolved solids greater than 500 mg/l will cause problems for people not used to consuming such high concentrations. Solids loadings, especially suspended solids, are used to design municipal treatment plants and evaluate the efficiency of a process.

10.5.2 Recommended Preservation and Handling Methods

10.5.2.1 Bromide * - Preserve all water and wastewater samples by refrigeration at 4°C. Hold grab samples for 24 hours and composite samples for 24 hours after the maximum composite interval or 48 hours total. Clean borosilicate glass or polyethylene containers using the techniques outlined in Section 3.4. Collect 250-500 mls of sample following the recommendations in Section 2.5.

10.5.2.2 Chloride * - Refrigerate samples for chloride analysis at 4°C and hold up to 14 days. If the samples are iced, the compositing interval is not critical. Clean polyethylene and borosilicate glass containers as outlined in Section 3.4. No special bottle preparation is required. Sample following the instructions in Section 2.5 and collect 50-200 mls.

10.5.2.3 Cyanide * - Add NaOH sample to pH greater than 12 and refrigerate samples for cyanide analysis. This technique prevents the losses of hydrogen cyanide for 24 hours. Analyze grab samples within 24 hours and composite samples within 30 hours (allowing 6 hours for sample transport). Clean polyethylene and borosilicate glass containers as recommended in Section 3.4. Collect samples prior to chlorination or

Parameter: Bromide (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 24 hours *

Composite Samples (After Composite Preparation) 24 hours * Max. Compositing Period 24 hours *

Container Type: Plastic or Glass

Volume: 250 - 500 ml

Preparation Method: None

Comments:

Parameter: Chloride (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 14 days

Composite Samples (After Composite Preparation) 12 days Max. Compositing Period 48 hours

Container Type: Plastic or Glass

Volume: 50 - 200 mls

Preparation Method: None

Comments:

Figure 10.16. Recommended preservation and handling methods - Br & Cl

Parameter: Cyanide (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Na OH addition to pH 12 or greater plus refrigeration at 4°C.

Maximum Holding Times

Grab Samples 24 hours *

Composite Samples (After Composite Preparation) 6 hours * Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 500 - 1000 mls.

Preparation Method: None

Comments: Sample before chlorine is added to the sample

Parameter: Fluoride (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 14 days

Composite Samples (After Composite Preparation) 12 days Max. Compositing Period 48 hours

Container Type: Plastic Only

Volume: 300 - 5-- mls

Preparation Method: None

Comments:

Figure 10.17. Recommended preservation and handling methods - CN^- & F^-

immediately remove chlorine to avoid reduction of cyanide to carbon dioxide and nitrogen gas. Collect 500-1000 ml following procedures outlined in Section 2.5.

10.5.2.4 Fluoride * - Polyethylene containers only are allowed for fluoride collection since fluoride is easily absorbed onto glass. Collect samples of 300-500 mls and refrigerate at 4°C for up to 14 days.

10.5.2.5 Sulfate * - Refrigerate samples at 4°C for 7 days. Clean borosilicate glass or polyethylene containers using the procedures outlined in Section 3.4. Collect a volume of 100-500 mls using the sampling methods discussed in Section 2.5.

10.5.2.6 Sulfide * - Add 2 ml/l of 1 normal zinc acetate to samples and refrigerate at 4°C. This will stabilize sulfide samples up to 7 days although the compositing interval must be limited to 24 hours unless the preservative is present in the bottle. Clean borosilicate glass or polyethylene as indicated in Section 3.4 and collect 300-500 ml.

10.5.2.7 Sulfite * - Collect a full sample bottle and cap immediately to reduce contact with oxygen. Refrigerate samples at 4°C in either polyethylene or borosilicate glass and analyze immediately or within 24 hours of sampling (grab) and 30 hours for composite (6 hour transport time). Collect 200-500 mls.

10.5.2.8 Acidity * - Refrigerate samples at 4°C and analyze grabs within 24 hours and composite samples within 48 hours. This short holding time will reduce changes in the carbonate - bicarbonate balance. Collect 100 ml of sample into polyethylene or borosilicate glass containers.

10.5.2.9 Alkalinity * - Follow the same procedures as Section 10.5.2.8.

10.5.2.10 Chlorine residual * - Analyze samples within 15 minutes of collection or note the interval between sampling and analysis. Use borosilicate glass containers only to avoid the loss of chlorine residual through reduction of contaminants on the container walls, and fill sample container to top to reduce changes in the chlorine residual.

Avoid exposure to sunlight and excessive agitation of the sample. Collect a volume of 200-500 mls. Do not use composites.

10.5.2.11 Color* - Refrigerate samples at 4°C for 24 hours (grab) or 48 hours for composites. The short holding time will reduce natural changes in color. Collect a volume of 100-200 ml of sample into clean borosilicate glass containers to prevent the adsorption of colored organics onto the container walls.

Parameter: Sulfate (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 7 days

Composite Samples (After Composite Preparation) 5 days Max. Compositing Period 48 hours

Container Type: Plastic or Glass

Volume: 100 - 500 ml (Depends on analytical method)

Preparation Method: None

Comments:

Parameter: Sulfide (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Addition of 2 ml/l 1 molar zinc acetate plus Refrigeration at 4°C

Maximum Holding Times

Grab Samples 7 days*

Composite Samples (After Composite Preparation) 6 days* Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 300 - 500 mls

Preparation Method: None

Comments:

Figure 10.18. Recommended preservation and handling methods - $SO_4^=$ and $S^=$

Parameter: Sulfite (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples Immediate analysis (24 hours or less)*

Composite Samples (After Composite Preparation) 6 hours maximum Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 200 - 500 mls

Preparation Method: None

Comments: Full sample and avoid contact with oxygen

Parameter: Acidity (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C*

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 24 hours Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 100 mls

Preparation Method: None

Comments:

Figure 10.19. Recommended preservation and handling methods-SO_3= and acidity

Parameter: Alkalinity (Primary - no alternate)*

Water or Wastewater:

X Municipal Wastewater	X Agricultural Runoff
X Industrial Wastewater	X Sludge
X Surface Water	X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 24 hours Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 100 mls

Preparation Method: None

Comments:

Parameter: Chlorine Residual (Primary - no alternate)*

Water or Wastewater:

X Municipal Wastewater	X Agricultural Runoff
X Industrial Wastewater	X Sludge
X Surface Water	X Sediment

Preservation Method:

Maximum Holding Times

Grab Samples Immediate analysis (less then 15 minutes)

Composite Samples (After Composite Preparation) not recommended Max. Compositing Period

Container Type: Glass only

Volume: 200 - 500 mls

Preparation Method:

Comments: Avoid exposure to sunlight or excessive agitation

Figure 10.20. Recommended preservation and handling methods - Alkalinity and Cl_2 Res.

Parameter: Color (Primary - no alternate) *

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff

X Industrial Wastewater X Sludge

X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 24 hours Max. Compositing Period 24 hours

Container Type: Glass

Volume: 100 - 200 mls

Preparation Method: None

Comments: Both apparent and true color are preserved in this manner

Parameter: Hardness (Primary - no alternate) *

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff

X Industrial Wastewater X Sludge

X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 7 days

Composite Samples (After Composite Preparation) 6 days Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 50 - 100 mls

Preparation Method: none

Comments:

Figure 10.21. Recommended preservation and handling methods - Color and Hardness

10.5.2.12 Hardness* - Refrigerate samples at 4°C and analyze within 7 days. Collect 50-100 mls into polyethylene or borosilicate glass containers. Follow this procedure when hardness is specifically analyzed, rather than a summation of metal ions.

10.5.2.13 Oil and Grease - Take sample into a solvent rinsed borosilicate glass container, add sulfuric acid to pH less than 2 and refrigerate at 4°C. Analyze the sample within 24 hours. Use a Teflon cap liner on all containers. Do not contact the sample with any plastic surfaces other than Teflon because it will absorb onto these other organic compounds. Collect a volume of 800 ml and analyze the entire contents. Take only grab samples for oil and grease analysis to avoid losses of the surface oil. A cylindrical sample which takes a cross-section of the stream is one acceptable technique. When this technique is not available, induce mixing with baffles, pumps, etc. to create a homogeneous flow stream. Then take sample directly into a solvent rinsed container.

10.5.2.14 pH * - Analyze samples on site whenever possible. Otherwise refrigerate samples at 4°C and analyze within 6 hours. After a composite is formed, analyze pH within 3 hours. Collect 50-100 mls for analysis in polyethylene or borosilicate glass containers. Keep containers closed prior to analysis to avoid unnecessary changes in the sample.

10.5.2.15 Phenolics * - Preserve samples for pheuol analysis by addition of 1g/l $CuSo_4$ plus H_3PO_4 to pH less than 4 and refrigerate at 4°C (1). Various preservatives have been tested with copper sulfate established as most effective (31). However, elimination of the possible precipitation of copper compounds at high pH, induced the use of additional acid. Analyze grab samples within 24 hours of sampling and composite samples within 24 hours of composite preparation. Borosilicate glass bottles only are acceptable due to background contamination or adsorption (32), especially at low concentrations. Collect a volume of 300-1000 mls and remove oxidizing agents immediately by the addition of ferrous ammonium sulfate.

10.5.2.16 Specific Conductance - Refrigerate samples at 4°C and analyze within 48 hours to 7 days depending on the biological activity of the sample. Use clean polyethylene containers (glass absorbs ions readily) to collect 100-250 mls.

10.5.2.17 Surfactants - Refrigerate samples at 4°C and analyze within 24 to 48 hours. Acid rinse polyethylene or borosilicate glass containers with nitric acid (see Section 3.4) prior to sample collection to remove residual detergents. Collect 500-1000 mls of sample

10.5.2.18 Turbidity - Refrigerate samples at 4°C and store in the dark. Analyze grab samples in 24 hours and composite samples in 48 hours. The short holding time will reduce changes in turbidity as colloidal material solubilizes. Use polyethylene or borosilicate glass containers to collect 100 mls of sample.

10.5.2.10 Total Solids - Refrigerate samples at 4° C and analyze samples within 7 days of sampling (25). Either polyethylene or borosilicate glass containers can be used to collect 100-250 mls of sample. Collect samples using isokinetic sampling with a vertically placed intake to obtain a cross-section of the stream.

10.5.2.20 Volatile Solids - Follow the same procedures used for Total Solids in Section 10.5.2.19.

10.5.2.21 Suspended Solids - Collect 200-500 mls of sample using isokinetic procedures through a vertically placed intake when possible, or sample only well mixed streams. Refrigerate samples at 4°C in clean polyethylene or borosilicate glass containers. Hold samples up to 7 days, however, biologically active samples may require analysis sooner to avoid changes in the sample from colloidal or other materials. Results from questionnaires (33) regarding current practices indicated that this may be needed for municipal wastewater influent, mixed liquor from activated sludge plants, agricultural runoff, biological sludges or other materials.

10.5.2.22 Total Dissolved Solids - Follow the procedures outlined for Suspended Solids in Section 10.5.2.21.

10.5.2.23 Preservation for Physical/Mineral Group - At least two samples must be taken into clean glass containers. A 1-liter sample should be preserved with sulfuric acid and refrigerated for analysis of oil and grease. Collect a second 1-liter sample and then immediately separate the aliquots for cyanide, phenolics and sulfite and add the appropriate chemical preservative. If transport time is greater than 15 minutes, analyze chlorine residual on site. If possible, *in situ* analysis of pH is recommended; otherwise measure pH of sample immediately upon receipt in the laboratory.

10.6 METHODS FOR PESTICIDES/HERBICIDES PARAMETER GROUP

10.6.1 Background

The use of pesticides to control diseases and increase food production is one of the important technical advances of the scientific community. However, the detrimental effects due to the accumulation of pesticides in fatty tissues of animals and plant waxes is causing environmental hazards and concern among many people. This problem is complicated because many

Parameter: Oil and Grease (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: H_2SO_4 addition to pH 2 plus refrigeration at 4^oC

Maximum Holding Times

Grab Samples 24 hours*

Composite Samples (After Composite Preparation) Not recommended Max. Compositing Period

Container Type: Glass/Solvent Rinse/Teflon liner

Volume: 800 mls

Preparation Method: None

Comments: Analyze entire volume directly from the sample containers

Parameter: pH (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4^oC

Maximum Holding Times

Grab Samples Immediate analysis (within 6 hours)

Composite Samples (After Composite Preparation) 3 hours Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 50 - 100 mls

Preparation Method: None

Comments: Samples bottle kept closed prior to analysis

Figure 10.22. Recommended preservation and handling methods - Oil and Grease and pH

Parameter: Phenolics (Primary - no alternate) *

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: 1 g/l $CuSO_4$ plus H_3PO_4 to pH less than 4 plus refrigeration at 4^oC

Maximum Holding Times

Grab Samples 24 hours *

Composite Samples (After Composite Preparation) 24 hours * Max. Compositing Period 24 hours *

Container Type: Glass

Volume: 500 - 1000 mls

Preparation Method: None

Comments: Remove oxidizing agents immediately by adding ferrous ammonium sulfate

Parameter: Specific Conductance (Primary - no alternate) *

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4^oC

Maximum Holding Times

Grab Samples 24 hours *

Composite Samples (After Composite Preparation) 24 hours * Max. Compositing Period 24 hours

Container Type: Plastic

Volume: 100 - 250 mls

Preparation Method: None

Comments:

Figure 10.23. Recommended preservation and handling methods - Phenolics and Sp. Cond.

Parameter: Surfactants - (Primary - no alternate) *

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 24 hours *

Composite Samples (After Composite Preparation) 24 hours * Max. Compositing Period 24 hours

Container Type: Glass or Plastic / HNO_3 Rinse

Volume: 500 - 1000 mls

Preparation Method: None

Comments:

Parameter: Turbidity (Primary - no alternate) *

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C (Store in dark)

Maximum Holding Times

Grab Samples 24 hours

Composite Samples (After Composite Preparation) 24 hours Max. Compositing Period 24 hours

Container Type: Plastic or glass

Volume: 100 mls

Preparation Method: None

Comments: Note of holding time exceeds 24 hours

Figure 10.24. Recommended preservation and handling methods - Surfactant and Turbidity

Parameter: Total Solids (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 7 days

Composite Samples (After Composite Preparation) 6 days Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 100 - 250 mls

Preparation Method: None

Comments:

Parameter: Volatile Solids (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 7 days

Composite Samples (After Composite Preparation) 6 days Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 100 - 250 mls

Preparation Method: None

Comments:

Figure 10.25. Recommended preservation and handling methods - Total and Volatile Solids

Parameter: Suspended Solids (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples Up to 7 days*

Composite Samples (After Composite Preparation) Up to 6 days* Max. Compositing Period

Container Type: Plastic or Glass

Volume: 200 - 500 mls

Preparation Method:

Comments: *Biologically active samples should be analyzed sooner

Parameter: Total Dissolved Solids (Primary - no alternate)*

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff
X Industrial Wastewater X Sludge
X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 48 hours* - 7 days

Composite Samples (After Composite Preparation) 24 hours* - 6 days Max. Compositing Period 24 hours

Container Type: Plastic or Glass

Volume: 200 - 500 mls

Preparation Method: None

Comments: *Biologically active samples should be analyzed sooner

Figure 10.26. Recommended preservation and handling methods - SS and TDS

types of pesticides resist degradation over long time periods and are not easily destroyed. There are several kinds of pesticides including organochlorine, organophosphorus and carbamate compounds. Of these types the chlorinated hydrocarbons have the longest half life. Therefore, many pesticide users have converted to less objectionable types of materials in their present applications. However, the previous accumulation of organochlorines still necessitates analysis for these compounds.

The short half life of the organophosphorus and carbamate problems is beneficial to the environment but it complicates preservation techniques if actual concentrations are to be measured. Table 10.4 shows the rate of disappearance of these pesticides in non preserved river water. The problem of disappearance is quite apparent.

Polychlorinated biphenyls (PCB's) are not pesticides, but they react similarly and have the same type of persistence. Use of PCB's has been widespread in the recent past as plasticizers in polyvinyl chloride, in brake linings, in varnish and in many other applications. Therefore the concentration of PCB's in the environmental remains significant.

10.6.2 Recommended Preservation and Handling Methods

10.6.2.1 General - Use glass containers specially prepared with a solvent rinse as outlined in Section 4.5. Whenever possible use empty solvent containers or similar bottles (34). This will reduce the possibility of contamination. Line cap with teflon liner.

10.6.2.2 Chlorinated Hydrocarbons and PCB's - Collect liquid samples into solvent rinsed narrow mouth glass jars and cover with Teflon[R] lined bakelite caps. A suitable bottle can be obtained by using an empty solvent container (34). Prepare the bottle by washing with a chromic acid rinse and solvent rinse. Refrigerate the sample and extract within one week. Collect grab samples following the procedures outlined in Section 2.5. Collect sludges and sediments in wide mouth containers for ease of handling. Freeze sludge or solids samples. These can be stored up to two months. Volume is dependent on the precision required and instrumentation involved.

10.6.2.3 Algicides - Since there are many varieties of algicides on the market, the following procedure should be followed:

1. Determine active agent in algicide.

2. Consult individual parameters and follow specific recommendations.

3. If active agent in unknown, follow procedures for Chlorinated Hydrocarbons and PCB's (Section 10.6.2.2).

10.6.2.4 Benzidine - Follow procedures outlined for Chlorinated Hydrocarbons and PCB's (Section 10.6.2.2).

Table 10.4. PERSISTENCE OF PESTICIDE COMPOUNDS IN RIVER WATER (35)

Compound	Original compound found[a], %				
	0-time	1 wk	2 wk	4 wk	8 wk
Organochlorine compounds					
BHC	100	100	100	100	100
Heptachlor	100	25	0	0	0
Aldrin	100	100	80	40	20
Heptachlor epoxide	100	100	100	100	100
Telodrin	100	25	10	0	0
Endosulfan	100	30	5	0	0
Dieldrin	100	100	100	100	100
DDE	100	100	100	100	100
DDT	100	100	100	100	100
DDD	100	100	100	100	100
Chlordane (tech.)	100	90	85	85	85
Endrin	100	100	100	100	100
Organophosphorus compounds					
Parathion	100	50	30	<5	0
Methyl parathion	80	25	10	0	0
Malathion	100	25	10	0	0
Ethion	100	90	75	50	50
Trithion	90	25	10	0	0
Fenthion	100	50	10	0	0
Dimethoate	100	100	85	75	50
Merphos	0	0	0	0	0
Merphos recov. as Def	100	50	30	10	<5
Azodrin	100	100	100	100	100
Carbamate compounds					
Sevin	90	5	0	0	0
Zectran	100	15	0	0	0
Matacil	100	60	10	0	0
Mesurol	90	0	0	0	0
Baygon	100	50	30	10	5
Monuron	80	40	30	20	0
Fenuron	80	60	20	0	0

[a] Pesticide concentrations were 10 μg/liter. Recoveries were rounded off to the nearest 5%.

Parameter: Chlorinated Hydrocarbon Pesticides and PCBs (primary)

Water or Wastewater:

X	Municipal Wastewater	X	Agricultural Runoff
X	Industrial Wastewater		Sludge
X	Surface Water		Sediment

Preservation Method: Refrigerate at 4°C

Maximum Holding Times

Grab Samples 1 week before extraction +

Composite Samples (After Composite Preparation) NA Max. Compositing Period

Container Type: Glass/ Teflon liner/ Solvent Rinse ++

Volume: 1,000 - 4,000 ml depends on instrument, concentrations

Preparation Method: None

Comments: + After extraction the holding time is indefinite

++ Cleaned and Empty Solvent Bottle Recommended

Parameter: Chlorinated Hydrocarbon Pesticides and PCBs (primary)

Water or Wastewater:

	Municipal Wastewater		Agricultural Runoff
	Industrial Wastewater	X	Sludge
	Surface Water	X	Sediment

Preservation Method: Freeze samples

Maximum Holding Times

Grab Samples 2 months - 6 months

Composite Samples (After Composite Preparation) - Max. Compositing Period ne

Container Type: Glass/ Widemouth/ Teflon liner/ Solvent Rinse

Volume: Depends on Concentration expected / Approx 100 grams dry weight solids

Preparation Method: None

Comments:

Figure 10.27. Recommended preservation and handling methods - pesticides and PCB's

Parameter: Benzidine

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff

X Industrial Wastewater X Sludge

X Surface Water X Sediment

Preservation Method: Refrigeration at 4°C

Maximum Holding Times

Grab Samples 1 week

Composite Samples (After Composite Preparation) _____ Max. Compositing Period _____

Container Type: Glass/Narrow mouth/ Teflon liner/Solvent Rinse

Volume: 1,000-4,000 ml depends on concentration/instrument

Preparation Method: None

Comments: _____

Figure 10.28. Recommended Preservation and Handling Methods - Benzidine

10.7 METHODS FOR THE BIOLOGICAL GROUP

10.7.1 Background

10.7.1.1 General - There are various biological parameters and many different analyses which can be performed on each species. Individual study objectives must be consulted prior to selection of the parameter and analysis which is to be done.

10.7.1.2 Fish - Fish investigations attract the most public attention due to the visibility of the organism and the public appeal. Fish are found in most natural waters and are used by man as a food supply and recreational resource. In the aquatic community fish exist at the peak of a food web and are indicative of the conditions of water quality.

10.7.1.3 Benthic Macroinvertebrate - This group is defined as those organisms living on or near the bottom which are retained by a U.S. standard #30 sieve. They occupy many stages of the food web and include herbivores, omnivores, carnivores and decomposers. Their usefulness in pollution studies is enhanced due to their limited mobility and comparably long life spans. The lack of mobility and sensitivity to stress allows their use for characteristics of recent pollution events.

10.7.1.4 Periphyton (Auwfuchs) - Periphyton include plants growing near or attached to solid surfaces and the semi-sessile and free living forms found within the attached mat. The periphyton community with the plytoplankton community are some of the primary producers of organic matter in the aquatic system. The community of periphyton become even more critical to the ecosystem in shallow areas. The community composition, however, is quite variable and depends on various factors such as water movement, depth, etc.

10.7.1.5 Phytoplankton - Phytoplankton are those forms of plankton which are able to carry on photosynthetic activities under proper conditions. These include chlorophyll bearing plants, primarily algae and usually constitute the greatest portion of the plankton biomass. The species composition of this community depends on many factors. One important aspect is the dependence on nutrient type and concentration which gives this community an indirect measure of the concentrations of these chemical parameters.

10.7.1.6 Macrophytes - This group includes large plants, primarily rooted, found in the aquatic ecosystem which can be seen without magnification. These are present in three growth forms: free floating, submerged and emergent. These plants cover large areas in shallow water and may interfere with navigation, migration and recreational uses of a water body.

10.7.1.7 Zooplankton - This is the portion of the plankton group made up of free-floating animal populations. These species are found at all depths of the water column and in both standing and flowing waters. They have the ability of independent movement and can alter their position in the water column.

10.7.1.8 Possible Analyses - Some common analysis techniques are briefly discussed below. The parameters most commonly analyzed for monitoring purposes are summarized in Table 10.5 (36).

1. Count and Identification - A useful test to determine overall the health of species in an ecosystem by providing data on standing crop and community structure.

2. Weight/length - The growth rate of a community is determined and compared to previous studies to indicate a change in water quality.

3. Flesh Tainting - A test of palatability to determine if sublethal chemical doses have imparted an unpleasant taste to fish or shellfish flesh.

4. Acetylcholinesterase - An indirect test of the previous effect of organophosphate pesticides on the central nervous system of fish in a water system.

5. Tissue Analysis - A qualitative or quantitative test of the concentration or histological effects of various materials including metals and pesticides in flesh.

6. Stomach Contents - An analysis of this will indicate the type and amount of feeding done by an organism prior to collection.

7. Wet, Dry and Ashfree Weight - These tests are used to make quantitative tests of the standing crop of a population.

8. Chlorophyll a - An estimate of the algal biomass is obtained which roughly indicates the standing crop.

9. ATP Determinations - ATP tests measure the total viable plankton biomass.

10. Diatom Species Proportional Count - This test indicates the health of a diatom community by comparing the results through the use of a diversity index.

Table 10.5. PARAMETERS OF BIOLOGICAL COMMUNITIES MOST COMMONLY ANALYZED FOR MONITORING PURPOSES (36)

Community	Parameter	Units
Plankton	Counts	Numbers/ml by genus and/or species
	Chlorophyll *a*	mg/m^3
	Biomass (ash-free dry weight)	mg/m^3
Periphyton	Counts	$Numbers/mm^2$
	Chlorophyll *a*	mg/m^2
	Biomass (ash-free weight)	mg/m^2
	Autotrophic index	$\frac{\text{Ash-free weight } (mg/m^2)}{\text{Chlorophyll } a \ (mg/m^2)}$
Macrophyton	Areal coverage	Maps by species and species associations
	Biomass (ash-free weight)	g/m^2
Macroinvertebrate	Counts	Grab — $number/m^2$ Substrate — number/sampler
	Biomass	g/m^2
	Toxic substances	mg/kg
Fish	Toxic substances	mg/kg
	Counts	Number/unit of effort, expressed as per shocker hour or per 100 feet of a 24-hour net set
	Biomass (wet weight)	Same as counts
	Condition	$K(TL) = \frac{10^5 \times \text{weight in grams}}{L^3 \text{ (length in mm)}}$

10.7.1.9 Preservatives - Various preservatives exist to maintain species in the desired conditions. The advantages and disadvantages of various types are indicated in Table 10.6 (37,38).

10.7.2 Recommended Preservation and Handling Methods

The recommended procedures have been included in Tables 10.7-10.12 (37,38). Follow the methods given for specific parameter type and the desired test method. Analysis of parameters sooner than the maximum holding time is advisable in most situations.

10.8 METHODS FOR RADIOACTIVE PARAMETER GROUP

10.8.1 Background

Radiation is not a biological or chemical parameter but rather a physical property. As such, it is not affected by temperature changes or recombination into different molecular species.

There are different types of radiation; those which are of general concern are those which are capable of causing ionization, that is, producing ions by ejection of orbital electrons from the atoms of the material through which they travel. Radiation can be divided into particulate radiation and electromagnetic radiation. For the purposes of this chapter only two types of particulate radiation will be considered, beta and alpha particles, and one type of electromagnetic radiation, gamma radiation.

The radioactive properties of radioactive waste materials do not lend themselves to stabilization or removal by the various chemical, physical or biological processes used to treat "normal" industrial wastewaters. Radioactive waste treatment only alters the chemical state and the only method which will render these materials "safe" is long-term storage. For these reasons samples of water and/or wastewater for gross alpha and gross beta determinations should be taken from areas suspected of being contaminated with these materials. Data from this type of analysis will help to determine if a radioactive contaminant is being discharged, and whether or not that discharge is significant. Some of the major pathways of introduction of these materials into the environment are as follows:

Nuclear Power Plants - Effluents from plant treatment operations are routinely discharged. Monitoring programs at nuclear power plants are regulated by the U.S. Nuclear Regulatory Commission (NRC).

Table 10.6. COMPARISON OF CHEMICAL PRESERVATIVES FOR BIOLOGICAL PARAMETERS

Chemical	Advantage	Disadvantage
General Preservation		
1. Formalin (5-10% formaldehyde)	Kills species; infinite holding period	Objectionable odor, can cause contraction or deflaggelation
2. 70% ethanol		Needs neutralization w/sodium tetraborate
3. 40% isopropyl	Safer & easier for analyst to use; same advantages as formalin	Can cause contractual reaction
4. Oxyquinoline (2% solution) (8-hydroxyquinoline sulfate)	Safer & easier for analyst to use; can be added as solid in premeasured packets; same advantages as formalin	Can cause contractual reaction
5. Merthiolate solution	Morphology & color of algae are retained; distinguish between zoo and phyto plankton longer	Does not produce a sterile sample
Additives		
6. Glycerin (added with 1, 2 or 3)	Prevents tissues from drying	--
7. Copper sulfate	Retains bluegreen color of algae	Stains other material; also toxic
8. Detergent	Lowers surface tension to prevent clumping or clinging to container walls.	
Stains		
9. Lugols's solution	Stains algae; aids settling by releasing gases	Samples stable only one year

Table 10.7. RECOMMENDED PRESERVATION AND HANDLING METHODS - BENTHIC MACROINVERTEBRATES

Item	Preservation	Holding Time	Container
Count and Identification	70% Ethyl Alcohol	1 Year	Glass or Plastic
Wet Weight	Refrigerate at 4°C or Ice.	Immediate to 24 hours	Glass or Plastic
Dry Weight	Refrigerat at 4°C or Ice.	Immediate to 24 hours	Glass or Plastic
Ash-free Weight	Filter and Refrigerate at 4°C.	6 Months	Glass or Plastic
Calorimetry	Refrigerate at 4°C or Ice. Once filtered, store in desiccator	Immediate to 24 hours	Glass or Plastic
Radio Tracer Studies	Freeze	1 Year	Glass or Plastic
Flesh Tainting	Freeze	Indefinite	Glass or Plastic
Tissue Analysis	Freeze	Indefinite	Glass or Plastic

Table 10.8. RECOMMENDED PRESERVATION AND HANDLING METHODS - FISH

	Preservation	Holding Time	Container
Count/Identification/	10% Formalin, add 3 gr. borax and 50 ml glycerin per liter *	Indefinite (1 year) (sooner is better)	Borosilicate Glass or Polyethylene
Weigh/Length	None - analyze immediately	None	None
Flesh Tainting	Clean then freeze	Indefinite	Borosilicate Glass or Polyethylene Aluminum Foil
Acetylcholinesterase	Freeze sample	Indefinite	Aluminum Foil
Tissue Analysis	Freeze sample	Indefinite	Borosilicate Glass of Polyethylene Aluminum Foil
Stomach Content	Remove stomach from fish and preserve in 10% Formalin (as #1)	Indefinite (1 year) (Prefer sooner)	Glass or Plastic

Comments - * Change solution to alcohol after 1 week

Table 10.9. RECOMMENDED PRESERVATION AND HANDLING METHODS - MACROPHYTES AND MACROALGAE

	Preservation Method	Holding Time	Container
Count and Identification	5% formalin	1 year	Plastic or Glass
Wet Weight	Refrigeration at $4^{o}C$ or Icing	Immediate-24 hours	Plastic or Glass
Dry Weight	Refrigeration at $4^{o}C$ or icing	Immediate-24 hours	Plastic or Glass
Ash-free Weight	Freeze	6 months	Plastic or Glass
Chlorophyll A	Freeze at -20°	1 month (keep out of light, acid)	Plastic or Glass

Table 10.10. RECOMMENDED PRESERVATION AND HANDLING METHODS - PERIPHYTON

	Preservation	Holding time	Container
Count and identification	5% neutral formalin	6 months	Opague, glass or plastic
Diatom species proportional count	5% neutral Formalin	6 months infinite	Glass or plastic
Wet and dry weight	Refrigerate at 4°C or ice (do not freeze)	Immediate to 24 hours	Glass or plastic
Ash-free weight	Freeze at -20°C	6 months	Glass or plastic
Chlorophyll Determination	Immediate extraction in 90% aqueous acetone, store at -20°C	1 month (keep out of light/ acid	Glass or plastic
ATP Determination	Extract by boiling with Tris Buffer and store extract at -20°C	6 months	Glass or plastic

Table 10.11. RECOMMENDED PRESERVATION AND HANDLING METHODS - PHYTOPLANKTON

	Preservation	Holding Time	Container
Count and Identification	a. 5% neutral Formalin b. Merthiolate	a. Indefinite b. One year	Opague, Plastic or Glass
Wet weight	Refrigerate at 4°C or ice sample (do not freeze)	Immediate to 24 hours	Plastic or Glass
Dry weight	Refrigerate sample at 4°C or ice	Immediate to 24 hours	Plastic or Glass
Ash-free weight	Filter and Freeze at -20°C	6 months	Plastic or Glass
Chlorophyll A	Extract immediately or filter and freeze in Desiccator -20°C	1 month (keep out of light/acid)	Plastic or Glass
Diatom species Proportional count	5% Formalin	6 months - Indefinite	Opague, Plastic or Glass
Calorimetry	Refrigerate at 4°C or ice Once filtered, store in desiccator	Immediate to 24 hours	Plastic or Glass
ATP Determination	Extract by boiling with Tris Buffer, freeze extract at -20°C	6 months	Plastic or Glass

Table 10.12. RECOMMENDED PRESERVATION AND HANDLING METHODS - ZOOPLANKTON

	Preservation	Holding Time	Container
Count and Identification	5% Formalin or Lugol's Solution plus 50% glycerin or 70% ethanol plus 50% glycerin	1 year	Glass or Plastic
Wet weight	Refrigerate at 4°C or Ice (do not freeze)	Immediate to 24 hours	Glass or Plastic
Dry weight	Refrigerate at 4°C or Ice (do not freeze)	Immediate to 24 hours	Glass or Plastic
Calorimetry	Refrigerate at 4°C or Ice (do not freeze). Once filtered, store in desiccator	Immediate to 24 hours	Glass or Plastic
ATP Determination	Immediately extract by boiling with Tris Buffer, store extract at -20°C	6 months	Glass or Plastic

Parameter: Radioactive Parameters

Water or Wastewater: X Municipal Wastewater X Agricultural Runoff

X Industrial Wastewater X Sludge*

X Surface Water X Sediment*

Preservation Method: HNO_3 addition to final concentration of 1%

Maximum Holding Times

Grab Samples Depends on half life of radionuclide*

Composite Samples (After Composite Preparation) Same as above Max. Compositing Period --

Container Type: Polyethylene or Teflon

Volume: Depends on expected concentration

Preparation Method: None

Comments: *Short lived radionuclides should be analyzed immediately

Figure 10.29. Recommended preservation and handling methods - Radioactive

Hospitals - These institutions use radioactive materials for various diagnostic and therapeutic procedures and small amounts of wastes are generated some of which are discharged to sanitary sewers. The discharges are regulated by the USNRC.

Processing of Uranium Ores - Installations which process uranium ore produce considerable volumes of wastes which are high in alpha emitters. This industry is also under the supervision of the USNRC.

Fuel Element Processing - This industry reprocesses fuel elements from nuclear power plants to recover unused fuel and to process the waste materials created by the fission process. The wastes produced by this process have extremely high levels of radiation and fall under the scrutiny of the USNRC.

Research Laboratories - These facilities sometimes use radionuclides for various techniques. Wastes may be discharged after being treated, stored, diluted, etc. These discharges are regulated by the USNRC.

10.8.2 Recommended Preservation and Handling Methods

Collect samples as indicated in Section 2.5. Collect a flow proportional composite sample whenever possible (39). The volume collected will vary with expected concentrations but a minimum of 1 liter should be obtained (40,41,42). Acceptable sample containers are polypropylene, polyethylene (41,43) or Teflon. Pretreat the sample container as follows (40,44):

a. Fill the container with concentrated nitric acid and leave stand for one day.

b. Rinse with detergent water.

c. Rinse twice with double distilled water.

Acidify sample to a final concentration of 1% acid using nitric acid (40,41). Analyze short lived radionuclides as soon as possible. If the species has a long half life, the holding time is not critical.

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CHAPTER 11

COLLECTING AND HANDLING MICROBIOLOGICAL SAMPLES

11.1 BACKGROUND

The control of fecal contamination from warm-blooded animals is a significant factor in the maintenance of public health. Pathogenic organisms which are normally present in municipal wastewaters can cause serious diseases and other health problems in the water supply or in waters used for recreational purposes.

Since monitoring plays such an important role in the control of pathogens, certain parameters have become recognized as indicators of the sanitary quality of a stream or water supply. The parameters most frequently used as indicators of pollution include standard plate count, total coliform, fecal coliform and fecal streptococci, as well as the pathogens themselves (e.g. Salmonella).

11.2 COMMON ANALYSES

11.2.1 Standard Plate Count

The standard plate count method "enumerates only that portion of the bacterial population that can grow under the conditions of the test, and usually constitutes only a small fraction of all the bacteria present" (1). The number of developing bacteria may vary greatly due to the influence of individual bacterial growth requirements. Some of these requirements include temperature, oxygen level, and nutrients present.

11.2.2 Coliforms

The coliform group may be subdivided into the two following categories (2):

1. Coliforms normally of fecal origin (primarily *E. coli* types).

2. Coliforms usually associated with vegetation and soils (primarily *E. aerogenes* and *E. cloacae*) as well as intermediates, all of which may occur in fecal matter but in smaller numbers than *E. coli*.

Standard Methods, 13th Edition (3) defines the coliform group as "all of the aerobic and facultative anaerobic, gram-negative, nonspore-forming, rodshaped bacteria which ferment lactose with gas formation within 48 hours at 35°C". The two analytical techniques recommended by EPA and Standard Methods for the enumeration of coliforms are the multiple tube and membrane filter methods (3,4). The microbiological standards for public water supplies and drinking waters are based solely on total coliform numbers.

Since many of the coliform organism groups originate from sources other than human and animal feces (5), water microbiologists distinguish the fecal from the nonfecal coliforms. The transition in recent years to the fecal coliform analysis as an indication of bacterial pollution is intended to provide a more accurate estimate of the sanitary quality of the water involved.

11.2.3 Fecal Coliforms

Fecal coliform organisms are defines as those coliforms "that ferment lactose with gas production within 24 hours at 44.5°C ± 0.2°C"(3). Research has shown this organism to be a reliable indicator of contamination of streams, municipal and industrial discharges, and recreational waters (6). No method is presently available which distinguishes human fecal coliforms from those of other warm-blooded animals.

The analytical techniques for identifying fecal coliforms in water are the multiple-tube fermentation method and the membrane filter technique. Both are described by Standard Methods, 13th Edition (3) and EPA's manual (4).

11.2.4 Fecal Streptococci

The role of fecal streptotocci as indicator organisms has recently been given more attention. Fecal streptococcal determinations may become an important asset in water pollution surveys on rivers and streams to distinguish whether the source of the contamination is animal or human.

The EPA manual (4) proposes the following definition of fecal streptococci:

> Fecal streptococci include the serological groups, D, Q and the viridans streptococci that are of sanitary significance and grow on KF streptococcus and PSE media and in azide destrose/EVA MPN media at 35°C.

The EPA manual (4) and Standard Methods, 13th Edition (3) have listed three methods of analysis: multiple tube technique (MPN), membrane filter technique (MF), and a plate count procedure.

11.2.5 Salmonella

Salmonella are a group of pathogenic microorganisms responsible for many waterborne-disease outbreaks. The absence of Salmonella does not indicate the absence of other pathogenic organisms. Generally, a large volume of sample is required to isolate this pathogen, as opposed to the relatively small volume needed for coliform and fecal coliform analysis. Salmonella have been isolated in sewage and stormwater.

A state-of-the-art approach to Salmonella identification is presented in Standard Methods (3) and in EPA's manual (4).

11.3 SAMPLE BOTTLE PREPARATION

Sample bottles must be resistant to sterilizing conditions and the solvent action of water. Wide mouth screw cap or ground glass stoppered bottles, or heat-resistant plastic bottles (preferably polypropylene) may be used provided they can be sterilized without producing toxic materials. Screw capped bottles must be equipped with neoprene rubber liners or other materials that do not produce bacteriostatic or nutritive compounds upon sterilization.

11.3.1 Selection and Cleansing of Bottles

Select bottles of sufficient capacity to provide a volume necessary for all analyses, but not less than 100 ml should be collected. Discard bottles which have chips, cracks, and etched surfaces. Bottle closures must be capable of creating a water-tight seal. Before use, thoroughly clease bottles and closures with detergent and hot water, followed by a hot water rinse to remove all traces of detergent. Then rinse three times with a good quality distilled water. A test for the biological examination of glassware where bacteriostitic or inhibitory residues may be present is described in EPA's manual (4).

11.3.2 Use of Dechlorinating and Chelating Agents

Add a dechlorinating agent to the sample bottle when water and wastewater samples containing residual chlorine are anticipated. Add sodium thiosulfate to the bottle before sterilization at a concentration of 0.1 ml of a 10 percent solution for each 125 ml (4 oz) sample volume (4).

Add a chelating agent to the sample bottle when samples suspected of containing >0.01 mg/l concentration of heavy metals such as copper, nickel, zinc, etc. Add 0.3 ml of a 15 percent solution ethylene diamine tetraacetic acid (EDTA) for each 125 ml (4 oz) sample volume prior to sterilization (7,8).

11.3.3 Wrapping of Bottles (4)

Protect the tops and necks of ground glass stoppered bottles from contamination by covering them before sterilization with aluminum foil or kraft paper. Screw-cap closures do not require a cover.

11.3.4 Sterilization of Bottles (4)

Autoclave glass or heat-resistant polypropylene plastic bottles at 121°C for 15 minutes. Glassware may be alternately sterilized in a hot air oven at 170°C for not less than one hour. Ethylene oxide gas sterilization is acceptable for plastic containers that are not heat resistant. Sample bottles sterilized by gas should be stored overnight before being used to allow the last traces of gas to dissipate.

11.4 SAMPLE COLLECTION

These sampling and procedural methods are applicable for sampling potable water, streams and rivers, recreational waters such as bathing beaches and swimming pools, lakes and reservoirs, marine and estuarine waters, shellfish harvesting waters, and domestic and industrial waste discharges.

In no case should a composite sample be collected for bacteriological examination. Data from individual samples, even though averaged, show a range of values. A composite sample will not display this range. Individual results will give information about industrial process variations. Also, one or more portions that make up a composite sample may contain toxic or nutritive material and cause erroneous results.

Collect samples by hand or with special devices if depth samples are required or if the sampling site is difficult to access such as bridges or banks adjacent to surface waters.

11.4.1 Surface Sampling by Hand (4)

Collect a grab sample directly into a sample bottle prepared as described in Section 11.3. Locate and then carefully identify the sampling site on a chain of custody tag, if this is required, a label, and a field log sheet (see Section 3.3). Remove the bottle coverings and closure and protect them from contamination. Avoid touching the inside of the closure. Grasp the bottle securely at the base with one hand and plunge the bottle mouth down into the water to avoid introducing surface scum. Position the bottle towards the current flow and away from the hand of the collector and the side of the sampling platform or boat. The sampling depth should be 15 to 30 cm (6-12 in.) below the water surface. An artificial current can be created, if the water body is static, by moving the bottle horizontally in the direction it is pointed and away from the sampler. Tip the bottle slightly upwards to allow air to exit and the bottle to fill. After removal of the bottle from the stream, pour out

a small portion of the sample to allow an air space of 2.5-5 cm (1-2 in.) above each sample for proper mixing of the sample before analysis. Tightly stopper and label the bottle.

11.4.2 Surface Sampling by Weighted Bottle Frame (4)

When sampling from a bridge or other structure above a stream or body of water, place the bottle in a weighted frame that holds the bottle securely. Remove the cover and lower the device to the water. It is preferable to use nylon rope which does not absorb water and will not rot. Face the bottle mouth upstream by swinging the sampling device first downstream, and then allow it to drop into the water, without slack in the rope. Pull the sample device rapidly upstream and out of the water, thus simulating the scooping motion of grab sampling. Take care not to dislodge dirt or other material from the sampling platform that might fall into the open bottle.

11.4.3 Depth Sampling (4)

Additional devices may be needed for collection of depth samples from lakes, reservoirs, estuaries and the oceans. Lower the depth sampler and/or container to the desired depth and open the device until full. Then closeand return to the surface. Although depth measurements are best made with a pre-marked steel cable, the sample depths can be determined by premeasuring and marking the nylon rope at intervals with a non-smearing ink, paint, or fingernail polish.

11.4.4 Potable Water Supplies (4)

The sanitary quality of potable water supplies has been recently established by the EPA Drinking Water Standards (9). These Standards emphasize the importance of a) collecting samples from properly distributed sampling sites, and b) repetitive sampling from single points. The sampling program includes examination of water as it enters and flows throughout the distribution system. For application of the Standards, the frequency of sampling and the location of sampling points shall be established jointly by the utility, the Reporting Agency, and the Certifying Authority. Additionally, the laboratory, the methods of analyses, and the technical competence of personnel shall be approved and inspected by the Reporting Agency and the Certifying Authority. (See 40CFR,141, National Interim Primary Drinking Water Regulations)

11.4.5 Water Distribution System Sampling (4)

Make certain the samples are not collected from spigots that leak or from spigots that contain aeration devices or screens within the faucet. For samples taken from direct water main connections, flush the spigot for five minutes to clear the service line. For wells equipped with hand or mechanical pumps, pump the water to waste for five minutes before the sample is collected. Remove the cap aseptically from the sample bottle.

Hold the sample bottle upright near the base while it is being filled. Avoid splashing at all times. Do not rinse the bottle with the sample, but fill it directly to within 2.5-5 cm (1-2 in.) from the top. Replace bottle closure and hood covering. Caution must be used to prevent contaminating the sample with finger, gloves or other materials. If the well does not have pumping machinery, collect the sample using a weighted sterilized sample bottle. Care must be taken to avoid contaminating the sample either with the surface scum from the water surface, or with dislodged material from the sides of the well.

11.4.6 Recreational Water Sampling

Collect samples daily during high use seasons--generally in the afternoon (10). Collect the samples at the most commonly used locations (e.g. bathing beach). Obtain samples of estuarine water at high tide, low tide and ebb tide to obtain the cyclic water quality deterioration.

11.4.7 Domestic and Industrial Waste Discharges (4)

It is often necessary to sample secondary and tertiary wastes from municipal waste treatment plants and various industrial waste treatment operations. In situations where the plant treatment efficiency varies considerably, collect grab samples around the clock at selected intervals for a three to five day period. If it is known that the process displays little variation, fewer samples are needed. In no case should a composite sample be collected for bacteriological examination. The NPDES has established wastewater treatment plant effluent limits for all dischargers. These are often based on maximum and mean values. A sufficient number of samples must be collected to satisfy the permit and/or provide statistically sound data and give a fair representation of the bacteriological quality of the discharge. (See 40CFR136, Guidelines Establishing Test Procedures for the Analysis of Pollutants.)

11.5 SAMPLE PRESERVATION AND HANDLING

The recommended preservation and handling methods are summarized in Figure 11.1.

11.5.1 Preservation Techniques

Immediately after collection, place the sample container in crushed ice or a refrigerator at 4°C (3). When crushed ice is used, transport the samples and ice in an insulated waterproof container. Do not use dry ice since it may freeze the sample.

11.5.2 Holding Times (3,4)

Hold the samples a maximum of 6 hours before analysis. If it is necessary to mail in samples, potable water samples can be held up to 30 hours before analysis.

Parameter: Total coliform, fecal coliform, fecal streptococci, Salmonella, Shingella, and standard plate count

Water or Wastewater:

x	Municipal Wastewater	x	Agricultural Runoff
x	Industrial Wastewater	x	Sludge
x	Surface Water	x	Sediment
		x	Drinking Water

Preservation Method: Refrigeration at 4°C or icing with crushed ice (do not freeze)

Maximum Holding Times

Grab Samples 6 hours with preservation, 30 hours with preservation for potable water

Composite Samples (After Composite Preparation) not recommended Max. Compositing Period _____

Container Type: Borosilicate glass; polyethylene, polypropylene/sterile/narrow mouth

Volume: 100-300 ml

Preparation Method: Sterilize containers

Comments:

1. For chlorinated waters, add 0.1 ml 10% sodium thiosulfate for each 125 ml of sample prior to bottle sterilization.
2. For waters with >0.01 mg/l heavy metals, add 0.3 ml 15% EDTA for each 125 ml of sample prior to bottle sterilization.

Figure 11.1. Recommended preservation and handling methods - microbiological parameters

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INDEX

Agricultural Discharges, 169-176
  Feedlot Discharges
    Frequency, 169-170
    Location, 170
  Field Runoff
    Frequency, 170
    Location, 170

Biological Parameters
  Common Parameters, 146
  Common Analyses, 146
  Preservation
    Types of Preservatives, 234
    Methods, 235-240

Chain of Custody, 43-53

Current Meters, 24

Demand Parameters
  Recommend Preservation, 196-201

Elbow Meters, 19

Flow Measurement
  In Pipes, 18-24
  In Open Channels or Sewers 24-33
  Primary Devices, 25-33, 35
  Municipal Wastewater, 143
  Industrial Wastewater, 143
  Surface Water/Bottom Sediment, 168
  Agricultural Discharges, 175
  Sludges, 181, 182

Flow Nozzle, 19, 20, 22

Freezing Samples, 42

Frequency of Sampling
  Method for Determining
    Using Spectral Analysis, 84-92
  Municipal Wastewaters, 125-128

  Industrial Wastewaters, 134

  Surface Waters/Bottom Sediments, 153, 154
  Agricultural Discharges, 169, 170
  Sludges, 180

Holding Time
  General, 57, Chapter 10

Icing, 252

Location of Sampling Points
  Segmentation Technique, 102-116
  Municipal
    Effluent Monitoring, 124
    In-Plant Locations, 129
  Sludges, 178, 180
  Industrial
    Effluent Monitoring, 135
    In-Plant Locations, 135
  Surface Waters
    Grid Method, 149
    Transects, 148
    Spatial Gradient Technique, 150
  Agricultural Runoff, 170

Location of Sampling Points (cont.)
Probability of Exceeding Standard, 117-118

Magnetic Flowmeter, 20

Manning Formula, 36

Mercury (II) Chloride
Use, 185-188

Metals
Recommended Preservation, 202-207

Microbiological Parameters
Common Types, 247-254
Bottle Cleansing, 249
Bottle Sterilization, 250
Recommended Preservation, 252, 253
Sample Collection, 250-252
Use of Chelating Agent, 249
Use of Dechlorinating Agent, 249

Nyquist Frequency, 65

Number of Samples
Methods for Determining
Based on Variability, 78-81
Based on Mean Value, 81-84
Municipal Wastewater, 129
Industrial Wastewater, 135
Surface Waters/Bottom Sediments, 150-153
Agricultural Runoff, 170
Sludges, 181

Nutrients
Recommended Preservation, 183-194

Oil and Grease
Preservation, 219-221
Sampling, 219

Orifice Meter, 21, 23

Palmer-Bowlus Flume, 32-33, 35

Parameters
Methods for Determining, 92-101
Correlation between Parameters, 95-101
Probability of Exceeding Standard, 93-94
To Analyze
Municipal, 127-129
Sludges, 178, 179
Industrial, 137, 138, 139
Surface Waters, 146
Agricultural Discharges, 170, 171

Parshall Blume, 30-33, 35, 131

Pesticides/Herbicides
Recommended Preservation, 226-229

Physical/Mineral Parameters
Recommended Preservation, 211-225

Pitot Tube, 20, 22, 25

Preservation and Handling
Municipal Wastewaters, 129
Surface Waters/Bottom Sediment, 168
Sludges, 181

Probability Distribution
Gaussian (Normal), 65-67
Pearson Type III, 66
Logarithmic, 68
Chi-Square, 68, 69
Student t, 70, 71
Determination of Type, 70-78

Radioactive Parameters
Defined, 232
Sources, 232, 241, 242
Recommended Preservation, 241, 242

Refrigeration, 42

Sample Containers
  Cleaning, 56
  Materials, 54, 55
  Preparation, 56, 242, 249, 250

Sample Identification, 42, 43

Samplers
  Automatic
    Criteria for Selection, 10-16
    Installation and Use, 16-18
    For Municipal Wastewaters, 130
    For Industrial Wastewaters, 142, 143
  Biological
    Water Samplers, 155
    Bottom Grabs, 156
    Coring Devices, 157
    Nets and Related Devices, 158
    Substrate Samplers, 164
  Agricultural Discharge, 172-174

Samples
  Type of:
    Grab, 4
    Composite, 4-9
    Municipal, 130
    Industrial, 137, 140
    Surface Waters/Bottom Sediments, 153
    Agricultural Discharge, 171
    Sludges, 181

Sampling Method
  Automatic, 10-18
  Manual, Guidelines, 37
  Municipal, 123
  Industrial, 133, 141
  Surface Waters/Bottom Sediments, 153
  Agricultural Discharges 171
  Sludges, 181

Sludges, Types, 177
  Sampling, 177-182

Spectral Analysis
  Definition, 64
  Municipal Wastewater Application, 129
  Industrial Wastewater Application, 134
  Agricultural Runoff, 170
  Method, 87-92

Ultrasonic Flowmeter, 20, 34, 35

Universal Preservative, 41, 42

Venturi Meter, 20, 22

Volumes of Samples
  General, 57
  Municipal Wastewater, 131
  Industrial Wastewater, 143
  Surface Water/Bottom Sediments, 168
  Agricultural Discharges, 170
  Sludges, 181

Weirs, 26-30, 33, 35